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A STUDY OF THE VAPOUR AND LIQUID PHASE BROMINATIONS OF ALKANES AND ELECTRONEGATIVELY SUBSTITUTED ALKANES

by

© TONY PAČE

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled A Study of the Vapour and Liquid Phase Brominations of Alkanes and Electronegatively Substituted Alkanes submitted by Tony Pace in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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TO CARMEN --

whose understanding, support, sacrifice
and love made the time spent on this work
a lot more pleasant and meaningful.

ABSTRACT

A general method for the evaluation of the kinetics of the vapour phase photobromination of alkanes and substituted alkanes was developed in order to obtain reliable values for the relative rates of abstraction by bromine atoms from these compounds, and to determine the relative rates of transfer of the alkyl radicals with bromine and with hydrogen bromide. The vapour phase bromination of a perdeuterated substrate was run in the presence of excess molecular bromine and excess hydrogen bromide. From a study of the brominated and protiated products formed, the relative rates of abstraction and of transfer were determined. The method was applied to the bromination of perdeuteriocyclohexane (a model for alkanes), perdeuterio-1-chlorobutane (a model for electronegatively substituted alkanes) and perdeuterio-1-bromobutane (a model for bromoalkanes). The kinetic data obtained from the perdeuterated substrates was found to describe very well the bromination of the natural, protiated compounds, showing that deuterium kinetic isotope effects were not important in the relative rates that were determined.

Transfer with hydrogen bromide occurs most readily in the bromination of perdeuteriocyclohexane, as

expected, since polar effects deactivate this reaction in the bromination of electronegatively substituted alkanes. This polar deactivation falls off as the distance of the radical centre involved from the substituent increases in the bromination of perdeuterio-1-chlorobutane.

The relative rates of bromination of cyclohexane and perdeuteriocyclohexane, and the relative rates of abstraction of the different hydrogens of 1-chlorobutane by bromine atoms were found to be the same in the vapour phase reaction run with minimal interference from the reversal reaction, and in liquid bromine solvent. This was taken as evidence that liquid bromine can scavenge all radicals, caged or "free", and that solution and vapour phase relative rates of the same kinetic order may be equated. At lower concentrations of molecular bromine, when the reversal reaction was not important, cage reversal between the geminate radical-hydrogen (or deuterium) bromide pair was proposed to explain the differences between the vapour and solution phase results.

In the liquid phase brominations in Freon 113, the relative rates of transfer of the alkyl radicals with bromine and with hydrogen bromide increased with increasing bromine concentration. This was attributed to reversal in solution with the new transfer species hydrogen tribromide.

The equilibrium constant of formation of this species was determined by nmr spectroscopy, and was consistent with the kinetics of the solution phase reactions.

The bromination of 1-bromobutane is complicated by elimination of bromine atoms from the β-bromobutyl radicals. In the vapour phase, the 1-butene thus formed is primarily brominated allylically. In solution, 1-butene adds bromine to produce 1,2-dibromobutane. The hydrogens β to the bromine substituent in 1-bromobutane are abstracted about five times faster than the γ-hydrogens at 25°, and the rate enhancement of the bromine substituent on the β-hydrogens is calculated as 10 over what would be expected on the basis of the polar effects of the substituent. No evidence for an enhanced rate of abstraction of the β-hydrogens of 1-chlorobutane was obtained in the bromination of this compound.

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INTRODUCTION

I.1 Homolytic Hydrogen Atom Abstraction

The abstraction of hydrogen atoms is the most common reaction that free radicals undergo. The reaction has been extensively studied, and two general effects have been observed that influence the reaction. The strength of the bonds being made and being broken and the polar influences on the transition state of the abstraction reaction both affect the rate and the position of attack on different molecules and on molecules that contain chemically different hydrogens.[1-12]

In every radical process studied, the rates of hydrogen atom abstraction from aliphatic alkanes increase on going from primary to secondary to tertiary C-H bonds. This order is independent of the nature of the attacking radical and is most easily explained as due to the strengths of the C-H bonds being broken. Thus, tertiary C-H bonds are the weakest, and tertiary hydrogens are abstracted at the fastest rates. The rate of attack on a particular C-H bond is also found to increase as the

H-X bond strength increases (reaction 1). For example, halogen atoms abstract hydrogen from methane or ethane in

$$RH + X\cdot \longrightarrow R\cdot + HX \qquad (1)$$

the order F>Cl>Br, i.e. the order of the hydrogen halide bond strengths.[5]

Two types of polar effects have been observed in free radical reactions. One of these, an inductive effect, is illustrated in the chlorination of electronegatively substituted butanes (Table 1). The relatively electronegative chlorine atom prefers attack on hydrogens furthest removed from the electronegative group. This effect has been rationalized by the assertion that in the transition state of the hydrogen abstraction reaction, there is electrostatic repulsion between the polar C-X bond of the butane and the H-Cl bond being formed. This effect falls off rapidly with distance from the substituent, and therefore attack on the γ-position is preferred over attack on the β-position.[8]

The second type of polar effect is a donor-acceptor type, and is exemplified in the bromination of substituted toluenes. The free radical reactions of bromine with ring substituted toluenes have been correlated well with the Hammett equation ($\rho=-1.36$ at 80° in carbon tetrachloride, correlation with σ^+).[16] In the transition

Table 1

Relative Reactivities in the Chlorination of Selected Substituted Butanes[a]

X ——	CH_2 ——	CH_2 ——	CH_2 ——	CH_3
CF_3[b]	0.04	1.2	4.3	1.0
F[b]	0.9	1.7	3.7	1.0
Cl[b]	0.8	2.1	3.7	1.0
FOC[c]	0.08	1.6	4.2	1.0
ClOC[c]	0.2	2.1	3.9	1.0
CH_3OOC[c]	0.4	2.4	3.6	1.0
CH_3COO[d]	0.1	2.1	3.9	1.0
CF_3COO[d]	0.2	1.3	3.6	1.0

[a] Reactivity in the gas phase at 75° per hydrogen atom relative to the primary δ hydrogen.

[b] Taken from ref. 13.

[c] Taken from ref. 14.

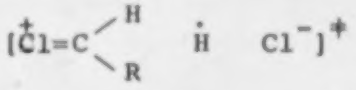
[d] Run at 100°; ref. 15.

state of these reactions, participation of resonance structures of the type **2a** must be important; in this

$$[\mathrm{Ar}^{+} \quad \dot{\mathrm{H}} \quad \mathrm{Br}^{-}]^{\ddagger}$$

2a

structure, an electron is transferred from the benzyl group to the bromine atom. This type of stabilization is also important in the abstraction of hydrogens from carbon atoms carrying atoms with lone pairs of electrons, e.g. in the chlorination of 1-chlorobutane at the α-position, structure **2b** adds to the stabilization



2b

of the transition state.[6,10]

Other effects, such as solvent and steric effects, do not generally greatly influence free radical hydrogen abstraction reactions. Thus, solvent effects are usually not important: though large effects have been reported for chlorinations in aromatic solvents, and smaller solvent effects are known for _tert_-butoxy radicals, there are usually only small differences between results obtained in the gas phase and in solution.[17,18] Mayo has reviewed gas and liquid phase free radical reactions, and concludes that though solvation effects may be important, they are not very significant for inert solvents, and tend to cancel out in competing reactions of the same kinetic order.[19]

Steric effects are also not very significant in hydrogen abstraction reactions:[6,20] even though tertiary aliphatic C-H bonds are the ones that are most sterically hindered, they undergo hydrogen abstraction at the fastest rates by all radicals. It has been suggested, though, that displacement on carbon, rather than displacement on hydrogen, is rare due to a high activation energy requirement caused by the sterically hindered approach of a free radical to an atom that is coordinated to two or more atoms or groups.[6]

I.2 Free Radical Bromination Reactions

Hydrogen abstraction by bromine atoms[21,22] is quite unique in free radical chemistry. The bromine atom is one of the most selective hydrogen abstracting species known; e.g. the primary:secondary:tertiary selectivities are 1:100:2000.[22] This selectivity is due to the fact that hydrogen abstraction by bromine for all but the weakest C-H bonds is endothermic. Bromine atoms are therefore very sensitive to small changes in the energetics of the reactions, and these small changes will be reflected in significantly increased or decreased rates of reaction.

By the Hammond principle,[23] the transition state for the endothermic bromination reactions should resemble most closely the products: consequently brominations are influenced strongly by donor-acceptor polar effects. This is illustrated by the large, negative Hammett ρ value for the free radical bromination of toluenes, and by the contrasting behaviour of cyclohexane and toluene to bromination and chlorination. In chlorination, cyclohexane reacts at a faster rate than toluene (k_c/k_t = 2.8 (per H atom, 80°)[24]); this was attributed to the electron withdrawing effect of the aromatic ring, since for the exothermic chlorination, there is no significant contribution of the resonance stabilization of the benzyl radical. However, for the less electronegative and more selective bromine atom, the situation is reversed; toluene brominates much faster than cyclohexane (k_t/k_c = 250 (per H atom, 80°)[24,25]), since the extensive bond breaking in the transition state for bromination leads to increased odd electron density at the benzylic position and considerable resonance stabilization due to the phenyl ring.

Due to their sensitivity to small changes in the activation energy, bromination reactions are also influenced by effects other than bond strengths and polar effects; these include reversible hydrogen atom abstraction, cage effects, complex formation, elimination of groups or atoms that are β to the radical, and anchimeric assistance by groups of atoms in the abstraction of hydrogens β to the group. These effects have either been shown to occur or have been proposed for free radical brominations, and are expected to complicate any mechanistic scheme for these reactions.

I.2.1. Reversible Hydrogen Abstraction

The effect of reversible hydrogen atom abstraction on the kinetics and on the products of the bromination of alkanes, aranes, and substituted alkanes and aranes has been a topic of considerable concern. As noted above, bromine atom attack on C-H bonds (reaction 3) is generally endothermic; the reversal reaction with hydrogen bromide (reaction 4) will therefore, in most cases, be exothermic, and though transfer of bromine to the carbon-centered radical (reaction 5) is always exothermic, the reversal reaction may compete with the product forming step.

$$RH + Br\cdot \xrightarrow{k_1} R\cdot + HBr \qquad (3)$$

$$R\cdot + HBr \xrightarrow{k_2} RH + Br\cdot \qquad (4)$$

$$R\cdot + Br_2 \xrightarrow{k_3} RBr + Br\cdot \qquad (5)$$

In their classic work on the bromination of methane, Kistiakowsky and Van Artsdalen[26] showed that hydrogen bromide inhibited the reaction, and they calculated that the methyl radical transferred about sixteen times faster with bromine than with hydrogen bromide at 37°. No inhibition, however, was observed in the bromination of bromomethane, implying that k_3/k_2 was greater than 100. Andersen,[27] Van Artsdalen,[28-30] and Sullivan[31] extended the studies of the absolute rates of brominations with molecular bromine to other simple substrates in the vapour phase (Table 2). In all the compounds studied, reversal with hydrogen bromide was important; in some cases it occured faster than transfer with bromine.

The transfer with hydrogen bromide in the bromination of chloroform has also been demonstrated in a chemical way by carrying out the vapour phase reaction of deuteriochloroform with added hydrogen bromide: the unbrominated chloroform was found to have incorporated a significant amount of protium. No incorporation was observed in the chlorination reaction with added hydrogen chloride, since the reversal reaction in this case must have an activation energy greater than 7.5 kcal./mol.[35]

Table 2

Relative Rates of Transfer of Selected Alkyl Radicals with Bromine (k_3) and with Hydrogen Bromide (k_2) in the Vapour Phase

Substrate	Temperature °C	BDE[a]	k_3/k_2[b]	Ref.
CH_4	37 - 210	104.0	15.6 - 4.8	26
CH_3Br	50 - 110	99[c]	Large	26
C_2H_6	35 - 95	98.0	14	27
$(CH_3)_3CH$	40 - 85	91.0	2.8 - 0.6	28
$(CH_3)_4C$	107 - 151	99.3	0.8 - 0.2	29
$C_6H_5CH_3$	90 - 133	85	1.7 - 0.8	30
$CHCl_3$	147 - 169	95.7	25.6 - 23.3	31

[a] Bond dissociation energy, taken from ref. 32 and 33.

[b] Some of these results have been critisized by Benson and Buss.[34]

[c] Taken from ref. 28.

Although the work on the determination of the absolute rates (Table 2) was carefully done and yielded acceptable values of the bond strengths, the results have been suspect because the A factors of the observed reactions were very high.[3] Benson and Buss[34] explained the discrepancies on the grounds that an assumption made in interpreting the results was invalid for the more reactive compounds. The necessary assumption was that steady state concentrations of bromine atoms were reached in times that were short compared with the lengths of the reactions. Benson and Buss calculated that a steady state was only attained for hydrocarbons less reactive than ethane. Although the magnitude of the relative rates reported (Table 2) may therefore be in error, the results show that hydrogen bromide reversal must be taken into account in any kinetic analysis of bromination reactions.

Transfer with hydrogen bromide has also been well documented in the bromination of toluene and substituted toluenes with a number of different brominating reagents. In this reaction, the reversal reaction is endothermic ($\Delta H = 2.5$ kcal./mol, $D(PhCH_2\text{-}H) = 85$ and $D(H\text{-}Br) = 87.5$ kcal./mol[32]). The deuterium kinetic isotope effect for the bromination of toluene-α-d_1 with bromine at 80° was reported by Urry[36] to be 3.3. A reinvestigation by Wiberg and Slaugh,[37] however, showed that under conditions of no hydrogen bromide reversal (either using N-bromosuccinimide (NBS) as a brominating agent, or sweeping out the hydrogen bromide formed in the reaction with a nitrogen stream), the isotope effect was 4.6; Wiberg attributed the difference to interference by the reversal reaction in Urry's work.

A similar effect was reported by Pearson and Martin on the magnitude of the Hammett ρ value for the bromination of substituted toluenes.[16] This value was determined by Kooyman, van Helden and Bickel[38] to be -1.05 (80°, correlation with σ^+). By maintaining the Br_2/HBr ratio large throughout the reaction, Pearson and Martin obtained a value for ρ of -1.36 (80°, correlation with σ^+),[16] which is in excellent agreement with the ρ value for NBS brominations of toluenes, -1.39[16] and -1.46[39] (80°, correlation with σ^+), where the hydrogen bromide is scavenged very rapidly by reaction with the NBS.

One of the most dramatic effects of hydrogen bromide reversal was recently reported in a study of the bromination reactions of bromotrichloromethane. These reactions have generally been accepted to proceed by a trichloromethyl radical chain.[5,6,22,40,41] Tanner et al. have now shown that this chain is dominant only in the presence of a hydrogen bromide scavenger (powdered potassium carbonate or ethylene oxide).[42,43] In "normal" bromotrichloromethane brominations, the major chain carrier is the bromine atom (reactions 6-8), and extensive reversal with hydrogen bromide takes place.

$$\mathrm{RH} + \mathrm{Br}\cdot \longrightarrow \mathrm{R}\cdot + \mathrm{HBr} \tag{6}$$

$$\mathrm{HBr} + \cdot\mathrm{CCl_3} \longrightarrow \mathrm{Br}\cdot + \mathrm{HCCl_3} \tag{7}$$

$$\mathrm{R}\cdot + \mathrm{BrCCl_3} \longrightarrow \mathrm{RBr} + \cdot\mathrm{CCl_3} \tag{8}$$

Most of the kinetic data reported for bromination reactions has been obtained from competitive reactions. Relative reactivity data is much more easily obtained than is absolute rate data, and is not influenced strongly by the method of initiation or the mode of termination (self-termination or trace impurities). Also, no assumption needs to be made about the rate at which steady state concentrations are attained. However, the relative reactivity method depends on the fact that in competitive reactions of two substrates R_aH and R_bH with a radical $Y\cdot$ (reactions 9, 10), the amount of reaction of each substrate can be determined from the amount of starting material at the end of the reaction, or from the

$$R_aH + Y\cdot \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} R_a\cdot + HY \xrightarrow[k_{ay}]{Y_2} R_aY \tag{9}$$

$$R_bH + Y\cdot \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} R_b\cdot + HY \xrightarrow[k_{by}]{Y_2} R_bY \tag{10}$$

amount of products formed from each reactant. The relative reactivity may then be calculated using equation 11.[6,11,22]

$$\ln([R_aH]^\circ/[R_aH]^f)/\ln([R_bH]^\circ/[R_bH]^f) = k_a/k_b \qquad (11)$$

Equation 11 can only be used when the abstraction reactions are irreversible: when reversible hydrogen atom abstraction takes place, equation 12 applies.[6,39,44] This equation contains a time dependent term, $[HY]/[Y_2]$, and consequently cannot be integrated.

$$\frac{d\ \ln[R_aH]/dt}{d\ \ln[R_bH]/dt} = \frac{k_a(1 + k_{-b}[HY]/k_{by}[Y_2])}{k_b(1 + k_{-a}[HY]/k_{ay}[Y_2])} \qquad (12)$$

The majority of the relative rates of bromination in the literature was obtained using equation 11, assuming (explicitly or implicitly) that no reversal took place; in most cases, however, no efforts were made to limit reversal or ascertain its absence.[44,45] Transfer with hydrogen bromide of radicals from different molecules, or of different radicals from the same molecule, will not necessarily occur at the same rate, as is apparent from the limited data in Table 2, and results obtained in the presence of hydrogen bromide should only be treated as apparent relative reactivities.

In comparing the rates of bromination of substituted and unsubstituted alkanes, the difference in the rates of reversal should be more pronounced, since the bromination of substituted alkanes is strongly influenced by polar effects. Thus, if one compares an electronegatively substituted alkane with the parent hydrocarbon, one would expect the substituted alkane to react with a bromine atom at a slower rate than the alkane, since no strong polar effects are expected in the transition state for abstraction of hydrogen from alkanes. However, by the principle of microscopic reversibility, the polar effects that influence the hydrogen abstraction from substituted alkanes must also be present in the reverse reaction with hydrogen bromide, and these will therefore decrease the reversal rate. The transfer with hydrogen bromide would then be more facile with the unsubstituted alkyl radical. If this reaction is important, the substituted alkane may appear to brominate at a faster rate than the parent hydrocarbon.

Tanner et al. studied this effect on the relative rates of bromination of electronegatively substituted butanes, 2-methylbutanes, and cyclohexanes under conditions of hydrogen bromide reversal ("normal" brominations, i.e. a 1:1:1 molar mixture of bromine and the two substrates) and conditions of limited reversal (using either an excess of N-bromosuccinimide in homogeneous acetonitrile solution or a large excess of liquid bromine), Table 3.[44] In most of the compounds studied, the negatively substituted alkanes reacted faster than the parent hydrocarbon in "normal" brominations. However, as the Br_2/HBr ratio was increased (Table 3), the rates of bromination of the substituted alkanes relative to the alkanes dropped, and when hydrogen bromide reversal was not important, most substituted alkanes brominated more slowly than their parent alkane.

I.2.2 Cage Effects

The concept of a solvent cage was first proposed by Frank and Rabinowitch,[46] and was extended and elaborated by Noyes.[47-49] The geminate radical pair is held in close vicinity by a cage of solvent molecules for about 10^{-10} second. Since concentration in the cage is about 10 M (bulk concentration), there will be a good likelihood of a cage reaction if the reaction rate is greater than 10^7 mol l^{-1}/sec.[1,50] The importance of cage reactions has been amply demonstrated in a number of reactions involving geminate radical pairs,[51] but little, if any, work has been done to investigate their occurrance in free radical substitution reactions, where the geminate pair is a radical-molecule pair.

Table 3

Comparison of the Relative Rates of Brominations Under Reversible and Irreversible Hydrogen Atom Abstraction (40°)[a]

Substrates R_1H	Substrates R_2H	Molar Ratio $R_1H:R_2H:Br_2$	k_{R_1H}/k_{R_2H}
1-Bromobutane	Cyclohexane	1:1:1	3.7 ± 0.3
		1:1:5	1.61 ± 0.12
		1:1:20	1.06 ± 0.04
		1:1:100	0.52 ± 0.01
		1:1:NBS[b]	0.58 ± 0.10
Chlorocyclohexane	Cyclohexane	1:1:1	1.48 ± 0.05
		1:1:20	0.68 ± 0.02
		1:1:100	0.36 ± 0.03
		1:1:NBS[b]	0.23 ± 0.02
Bromocyclohexane	Chlorocyclohexane	1:1:1	4.4 ± 0.1
		1:1:5	2.7 ± 0.02
		1:1:NBS[b]	1.8 ± 0.02
Bromocyclohexane	*Trans*-4-*tert*-butylbromocyclohexane	1:1:1	3.23 ± 0.01
		1:1:30	2.56 ± 0.02
		1:1:NBS[b]	1.92 ± 0.05
Cis-4-*tert*-butylbromocyclohexane	Bromocyclohexane	1:1:1	5.6 ± 0.6
		1:1:20	3.7 ± 0.4
		1:1:30	2.8 ± 0.2
		1:1:NBS[b]	2.1 ± 0.5

continued.....

Table 3 (cont'd.)

[a] Taken from ref. 44.

[b] Photoinitiated reactions of $R_1H:R_2H:NBS$ of 1:1:8 in acetonitrile homogeneous solution.

Haag and Heiba in 1965 suggested the possibility of a cage reaction between the alkyl radical and a molecule of bromine formed in immediate proximity on abstraction with $Br_3^{\cdot}$ (reaction 13).[52] This suggestion

$$RH + Br_3\cdot \longrightarrow (R\cdot + HBr + Br_2) \longrightarrow RBr + HBr + Br\cdot \qquad (13)$$

was made to explain the retention of optical activity in the bromination of some optically active substituted alkanes. Cage reaction between the geminate radical-hydrogen bromide pair has also been suggested to compete with diffusion from the cage.[44,53]

The reaction of a carbon-centered radical with bromine (reaction 5) has been generally accepted to have zero or very small activation energy, and has been accepted to be in the diffusion controlled range in solution.[21,22, 26-30,54] This assumption must be nearly correct since the reported vapour phase values of E_a and A assigned to this process will place the solution reaction, within one or two orders of magnitude, in the diffusion controlled range.[22,34,54] Since hydrogen bromide reversal is competitive with transfer with bromine,[28-30,37-44] reaction 4 will also be close to the diffusion controlled range.

In comparing the reactivity of different C-H bonds, if the rates of the cage reactions are competitive with those of diffusion, and the rates of the cage reactions are different, cage filtering will occur, i.e. the ratio of radicals escaping from the cage will be different from the kinetic distribution of radicals formed on abstraction. For example, for the competitive reaction of R_aH and R_bH with the radical $Y\cdot$ (reactions 9-10), if k_{-a} and k_{-b} are dissimilar and are competitive with diffusion, k_d and k'_d (reactions 14-15), the rate of dissappearance of

$$R_aH + Y\cdot \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} (R_a\cdot + HY) \xrightarrow{k_d} R_a\cdot \longrightarrow \text{products} \qquad (14)$$

$$R_bH + Y\cdot \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} (R_b\cdot + HY) \xrightarrow{k'_d} R_b\cdot \longrightarrow \text{products} \qquad (15)$$

starting materials will be given by expression 16 if there is no external reversal, and by expression 17 when external reversal takes place, where $[HY]^c$ is the cage concentration of HY (see Appendix 1).[55]

$$\frac{d\ \ln[R_aH]/dt}{d\ \ln[R_bH]/dt} = \frac{k_a(k_{-b}[HY]^c + k'_d)}{k_b(k_{-a}[HY]^c + k_d)} \qquad (16)$$

$$\frac{d\ \ln[R_aH]/dt}{d\ \ln[R_bH]/dt} = \frac{k_a k_d k_{ay}(k_{-b}[HY]^c + k'_d)}{k_b k'_d k_{by}(k_{-a}[HY]^c + k_d)} \bullet \frac{(k_{-b}[HY] + k_{by}[Br_2])}{(k_{-a}[HY] + k_{ay}[Br_2])} \qquad (17)$$

The term $(k_{-b}[HY]^c + k_d')/(k_{-a}[HY]^c + k_d)$ is related to the cage effect, and as long as the rate of reversal is comparable to that of diffusion, cage filtering will influence the relative rate of reaction of the two reactants. This will be the case for reversal with hydrogen bromide, and therefore cage reactions may play an important role in free radical bromination reactions, and further complicate solution phase brominations.

I.2.3 Complex Formation

Three types of complexing may occur in free radical brominations: self-complexing, or agglomeration, of the bromine, complexing between bromine and substrates or products, and complexing between bromine and the solvent.

No self association of bromine molecules has been reported in the literature.[56] Thus, the position of the absorption maximum in the visible spectrum of bromine solutions in organic solvents or of liquid bromine is very near to that of the maximum observed for gaseous bromine.[57] This has been taken as evidence against self-association or association with the solvent. However, Mulliken[58] has suggested that the presence of a second band at 290 mμ found in aromatic solutions is due to the charge-transfer spectrum of a 1:1 complex, analogous to the well established iodine complexes, although this band has been attributed to other effects.[59]

Some evidence is available for complexing between bromine and other compounds. A number of polyhalides are well known,[60] including hydrogen tribromide,[61,62] which may be considered as a complex between bromine and hydrogen bromide, one of the products of any bromination reaction. Complexing between alkyl iodides or bromides and bromine is also indicated by the pronounced light absorption in the 300-350 mμ region of solutions of bromine in these alkyl halides. Keefer and Andrews attributed this absorption to a 1:1 complex, although they noted that the complexing was rather weak compared to that of iodine with alkyl halides.[63]

Haag and Heiba proposed that the abstracting species in free radical brominations may be $Br_3\cdot$;[52] this is not unlikely since bromine is known to complex with chloride, bromide and iodide ions,[60] and on abstraction of hydrogen, $Br_3\cdot$ forms HBr_3, a known species. Little work has been done to investigate the role of complexing in homolytic brominations.

I.2.4 Elimination of the Substituent

Elimination of the substituent in the bromination of electronegatively substituted alkanes has also been reported, and this may further complicate any study of the mechanism. Thus, bromination of 1-fluoro-2-methylbutane or 2-methyl-1-butyl acetate with molecular bromine gave 1,2-dibromo-2-methylbutane as the major product.[53] An acid catalyzed elimination of fluorine from 1-fluoro-2-methyl-2-butyl radicals or of acetic acid from 2-bromo-2-methyl-1-butyl acetate has been suggested to account for the results. This mechanism is supported by Tedder's report that the vapour phase chlorination (Table 1) or bromination of 1-fluorobutane[13] and butyl acetate[15] gives no 1,2-dichloro or 1,2-dibromobutane. Also, when the bromination of 2-methylbutyl acetate was carried out in the presence of a hydrogen bromide scavenger (N-bromosuccinimide), no 1,2-dibromide was detected.[64]

Elimination of bromine from β-bromoalkyl radicals is a well known reaction and occurs very readily;[1,5,6,22] it is responsible for the rapid isomerization of alkenes by bromine atoms. Chlorination of bromocyclohexane gives 1,2-dichlorocyclohexane (5%), which probably arises from addition of chlorine to cyclohexene.[65] Similarly, elimination of bromine was reported in the chlorination of 1-bromobutane, in both liquid[66] and gas phase,[13] where 1,2-dichlorobutane was formed. Bruylants et al. brominated 1-bromobutane labelled with bromine-82 with molecular bromine in carbon tetrachloride to study the importance of elimination in solution.[67] After >87% conversion of the bromine, 3% of the total radioactivity was present in the inorganic products. Also, when the product 1,2-dibromobutane was dehydrobrominated, [illegible]% of the label was found at the 2-position.

These results may be analyzed further. If it is assumed that the scrambling of the label in 1,2-dibromobutane was due to an elimination-readdition mechanism instead of the rearrangement mechanism proposed by the authors, limits may be placed on the amount of β-bromobutyl radicals that eliminated a bromine atom. Since there were equal chances of the radioactive bromine adding to either end of the double bond, a minimum of 20% elimination is required to explain the rearrangement. To take into account the radioactivity in the inorganic products as well, the minimum is raised to 23%.

The maximum amount of elimination may be calculated by simulating the reaction where the Br-82 that was eliminated mixed completely with the bromine pool[68-74] prior to any other reactions. From the data in the communication, the fraction of bromine atoms that attacked 1-bromobutane at the 2-position was calculated as 0.8. It was assumed that this fraction was constant throughout the reaction (an assumption that is most likely not correct), and the bromination was simulated in 1000 steps (see Appendix 2). When 37% of the β-bromobutyl radicals eliminated bromine atoms, 10% of the Br-82 in 1,2-dibromobutane was calculated to be at the 2-position. At this fraction of elimination, it was calculated that 8% of the total radioactivity should have been in the inorganic products. The reported amount (3%) is smaller than this. It is possible that the reported figure may be in error, since the method used to determine the radioactivity in the organic compounds (using a tandem glpc-ionization chamber) appears to be more reliable than that used for the inorganic products (trapping these at the head of the glpc column on potassium hexacyanoferrate II, and then counting the solid).

The bromination of a number of bromoalkanes with bromine-81 has been studied in these laboratories to determine the importance of elimination from different β-bromoalkyl radicals (Table 4). A direct substitution mechanism predicts that the dibromides should contain 27.3% Br-79 and 72.7% Br-81. If olefin were formed during the reaction, some enrichment of the vicinal dibromides in bromine-81 was expected.[75,76] 1,2-Dibromobutane, 1,2-dibromocyclohexane and _cis_-1-_trans_-2-dibromo-4-_tert_-butylcyclohexane (see Table 4) were found to contain approximately 27% Br-79, showing that no overall enrichment had occurred. However, an analysis of the mass spectral intensities of the molecular ion peaks of these dibromides showed that these were not in the ratio predicted by this mechanism. For two bromine atoms with isotopic ratios of Br-79 and Br-81 of a, b and a', b', the ratio of the mass spectral peak intensities may be calculated from the expansion of the expression $(a + b)(a' + b')$.[77] A direct substitution mechanism requires that the dibromides contain the original bromine atom (Br-79:Br-81 = 0.51:0.49) and a second bromine atom from the molecular bromine (Br-79:Br-81 = 0.04:0.96), and therefore the intensities of the parent peaks in the mass spectrum should be in a ratio of 1:25:24. This was not the case for any of the dibromides studied; the dibromides therefore were not formed exclusively by direct substitution with the

Table 4

Bromination of Some Bromoalkanes with Bromine Enriched in Bromine-81[a,b]

Product	Mass Spectral Peaks[c]			Bromine Content		Isotopic Ratio of	
	79,79	79,81	81,81	Br-79	Br-81	Bromine Atom 1[d]	Bromine Atom 2[d]
			A. 1-Bromobutane				
1,2-Dibromobutane	1.0	10.8	12.7	0.26	0.74	0.43 : 0.57	0.10 : 0.90
1,3-Dibromobutane	1.0	5.8	5.1	0.33	0.67	0.48 : 0.52	0.18 : 0.82
			B. Bromocyclohexane				
Trans-1,2-dibromocyclohexane	1.0	8.9	10.2	0.27	0.73	0.42 : 0.58	0.12 : 0.88
			C. *Cis*-4-*tert*-butylbromocyclohexane				
Cis-1-*trans*-2-dibromo-4-*tert*-butylcyclohexane	1.0	6.6	8.4	0.27	0.73	0.37 : 0.62	0.17 : 0.83
Hydrogen Bromide[e]	-	-	-	0.18	0.82	--	--

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[a] Bromine was 96.04% bromine-81 and 3.96% bromine-79; taken from ref. 76.

[b] Run in the liquid phase at 40°.

continued.....

Table 4 (cont'd.)

[c] Intensities of the parent peaks relative to the 79,79 peak.

[d] Reported as Br-79 : Br-81.

[e] Analyzed as bromocyclohexane after reaction with cyclohexene.

the original molecular bromine pool, although, for the vicinal dibromides, the overall Br-79:Br-81 ratio was, coincidentally, that predicted for direct substitution.

From the relative intensities of the mass spectral peaks, the isotopic ratio of the two bromine atoms in the dibromides could be calculated (see Appendix 3). The results are given in Table 4. It is apparent that the vicinal dibromides could not have been formed exclusively by a direct substitution mechanism, since none of these compounds contained the original bromine atom of the bromoalkane (Br-79:Br-81 = 0.507:0.493). In all cases, the two bromine atoms were enriched in bromine-81; bromine from the molecular bromine pool had therefore been introduced into the two positions of the vicinal dibromides.

These results indicated that a scrambling mechanism was operating to introduce bromine-81 into the vicinal dibromide. This was attributed to an elimination-readdition mechanism, whereby some of the β-bromoalkyl radicals eliminated bromine atoms to give alkene. These bromine atoms (isotopic ratio 0.51:0.49) mixed rapidly with the bromine pool (i.e. the molecular bromine and hydrogen bromide in the reaction mixture)[68-74] thereby introducing bromine-79 into this pool. The alkene then added bromine; the vicinal dibromide formed in this way had therefore lost the original bromine atom of the starting bromoalkane.

Due to this elimination, the molecular bromine pool was enriched in bromine-79 as the reaction progressed. This was substantiated by the isotopic ratio of the hydrogen bromide formed in the bromination of *cis*-4-*tert*-butylbromocyclohexane (Table 4). The Br-79:Br-81 ratio was 0.18:0.82, greatly different from that of the starting molecular bromine (0.04:0.96). Similarly, 1,3-dibromobutane, formed in the bromination of 1-bromobutane (Table 4), had an excess of Br-79 over that predicted by direct substitution from the original bromine pool. In the case of this product, the radical centre was two atoms removed from the bromine substituent, and therefore elimination could not take place. These results were expected from the increased Br-79 content of the bromine pool as a result of elimination from the β-bromoalkyl radicals.

Since 1,3-dibromobutane must have been formed by direct substitution from the bromine pool, it was expected that this product would still contain the original bromine atom of the starting 1-bromobutane. However, both bromine atoms of this compound were enriched in bromine-81 (Table 4). This implied that part of the olefin that was formed added hydrogen bromide rather than bromine to give 1-bromobutane enriched in bromine-81. This was then brominated to give 1,3-dibromobutane enriched in bromine-81 at the 1-position.

The bromination of 2-bromobutane with bromine-81 has been studied in detail in these laboratories.[64] The starting material and the products were anlayzed for the isotopic ratio of the bromine after the reaction; 2-bromobutane had a Br-79:Br-81 ratio of 0.492:0.508, showing that it had incorporated Br-81 during the reaction. This was attributed to addition of hydrogen bromide to 2-butene formed by elimination of bromine atoms from the 3-bromo-2-butyl radicals. The hydrogen bromide was found to be highly enriched in bromine-79 (Br-79: Br-81 = 0.172:0.828), substantiating this conclusion. The vicinal dibromides (meso- and dl-2,3-dibromobutane) were enriched in bromine-81 (0.223:0.777 and 0.216:0.784 respectively), while 2,2-dibromobutane was enriched in bromine-79 (0.295:0.705). 1,2-Dibromobutane was also formed in this reaction, and it was highly enriched in Br-81 (0.125:0.875), showing that most of this product was formed by addition of bromine to 1-butene.

The fraction of vicinal dibromide that was formed by addition of bromine to the alkene could be calculated for 1-bromobutane and 2-bromobutane (see Appendix 3). For 1-bromobutane, e.g., the 1,2-dibromobutane that was formed by direct substitution must have had the same Br-79:Br-81 content as the 1,3-dibromobutane. The 1,2-dibromobutane formed by addition of bromine to 1-butene had both bromine atoms coming from the bromine pool; these were assumed to be the same as the second bromine atom in 1,3-dibromobutane (i.e. Br-79:Br-81 = 0.18:0.82, Table 4). From the final Br-79:Br-81 content of the vicinal dibromide (0.26:0.74), the fraction of 1,2-dibromobutane that was formed from olefin, and consequently the fraction of β-bromobutyl radicals that eliminated bromine atoms, was calculated to be 0.45. This result is in good agreement with the reanalysis of Bruylant's bromination of 1-bromobutane labelled with Br-82, where it was calculated that between 23-37% of the β-bromobutyl radicals eliminated bromine atoms prior to any further reaction.

Though elimination of bromine atoms in the bromination of bromoalkanes should not effect the relative rates of abstraction of the different hydrogen atoms from these substrates, if hydrogen bromide reversal is important, the two effects together may influence the product distribution obtained in the reactions. It has been suggested that the initially formed radicals undergo rapid reversal with hydrogen bromide; when the radical formed is β to the bromine substituent, it has the additional possibility of elimination of a bromine atom to give olefin. The olefin would add bromine rapidly to give vicinal dibromide. The net result of these reactions would be an increase of the vicinal dibromide over the other dibromides.[78]

I.2.5 Anchimeric Assistance

A further complication arises in the bromination of bromoalkanes and of chloroalkanes. Bromoalkanes are known to give abnormally large amounts of vicinal dibromides in free radical bromination with molecular bromine; e.g. bromination of bromocyclopentane or bromocyclohexane gives more than 90% 1,2-dibromocycloalkane.[66] These results are contrary to what is expected on the basis of polar effects (cf. Table 1), and anchimeric assistance by the bromine substituent in the abstraction of the β-hydrogens has been proposed to rationalize these anomalous results,[66,79-81] although this explanation has been questioned recently.[44,53,75,78,82-85] Anchimeric assistance has also been proposed in the bromination of some chloroalkanes,[79,86,87] although the evidence is less extensive than for bromoalkanes. The question of anchimeric assistance will be discussed in the section on 1-bromobutane.

I.3 Scope of this Thesis

For any understanding of the details of the mechanism of solution phase bromination reactions, it is necessary to know the relative importance of the effects delineated in section I.2. In order to simplify the mechanism of bromination, a study of the vapour phase bromination of three model compounds was undertaken. By carrying out the reaction in the gas phase, complications due to cage effects are removed, and complexing between bromine and bromine (e.g. $Br_3\cdot$) or the substrates or products would be unimportant due to the low concentrations normally used in gas phase reactions. The vapour phase reactions should thus be mainly affected by hydrogen bromide reversal, by polar effects, and by elimination, when this can take place. By comparison of the results in the vapour phase with those obtained in solution, the importance and magnitude of cage and complexing effects could then be determined.

A general method for the evaluation of the kinetics of the gas phase photobromination of alkanes and substituted alkanes was developed, and the method was applied to the bromination of cyclohexane, 1-chlorobutane and 1-bromobutane and their perdeuterated analogues. The bromination of cyclohexane, which was used as a model alkane, is only influenced by reversible hydrogen atom abstraction, since the cyclohexyl radical is not polar, and β-elimination cannot occur. The relative rates of bromination of cyclohexane and perdeuteriocyclohexane under conditions of negligible reversal were also determined, so that by comparison with the analogous result in solution, the magnitude of the cage effect on the bromination of cyclohexane could be determined.

1-Chlorobutane was studied to investigate quantitatively the effect of an electron withdrawing substituent on the rate of reversal relative to that of product formation. Since 1-chlorobutane contains different C-H bonds, the relative rates of abstraction of these hydrogens were also determined to investigate the polar effect along the molecule and establish the importance of anchimeric assistance in the abstraction of the β-hydrogens. Elimination was not anticipated to be important in this reaction, since β-chloroalkyl radicals give alkene only at elevated (~200°) temperatures.[21]

1-Bromobutane was studied as model for bromoalkanes. Other than polar and reversibility effects, elimination of bromine from the β-bromobutyl radicals and anchimeric assistance could be expected to complicate the bromination.

RESULTS AND DISCUSSION

II.1 Method for Determining Relative Rates of Bromination

Under "normal" bromination conditions, reversal of an alkyl radical with hydrogen bromide regenerates starting material, and therefore the reversal reaction can only be detected kinetically or by its stereochemical consequences (e.g. racemization of starting material, if this were optically active[53]). In the work on the absolute rates of bromination of simple alkanes, the rate of transfer of the alkyl radicals with hydrogen bromide was determined from a comparison of the rate of bromine consumption in reactions with and without added hydrogen bromide.[26-31]

The reversal reaction may be studied directly by carrying out the photobromination of perdeuterated substrates in the presence of excess hydrogen bromide (reactions 18-21). Under these conditions, the ratio of

$$\mathrm{RD} + \mathrm{Br} \longrightarrow \mathrm{R}\cdot + \mathrm{DBr} \qquad (18)$$

$$\mathrm{R}\cdot + \mathrm{DBr} \longrightarrow \mathrm{RD} \quad \mathrm{Br}\cdot \qquad (19)$$

$$\mathrm{R}\cdot + \mathrm{HBr} \xrightarrow{k_{-1}} \mathrm{RH} + \mathrm{Br}\cdot \qquad (20)$$

$$R\cdot + Br_2 \xrightarrow{k_2} RBr + Br\cdot \qquad (21)$$

the rate of transfer of the alkyl radical with bromine and with hydrogen bromide is independent of the concentration of the alkyl radical. When the reaction is stopped at low conversion of the perdeuterated substrate, where multiple exchange (D for D or H for H) is not important, the concentration of deuterium bromide will be very small compared to that of hydrogen bromide; coupled with the unfavourable isotope effect for reaction 19, this makes reversal with deuterium bromide uncompetitive with reversal with hydrogen bromide, and therefore reaction 19 may be neglected.

The rate of formation of brominated product, RBr, relative to the rate of formation of protiated substrate, RH, is given by equation 22. This expression, under the conditions described above (high concentrations

$$\frac{d[RBr]/dt}{d[RH]/dt} = \frac{k_2[Br_2]}{k_{-1}[HBr]} \qquad (22)$$

of bromine and hydrogen bromide, and low conversion of the substrate, where the concentrations of the transfer agents do not change significantly during the reaction), may be integrated and rearranged to give expression 23.

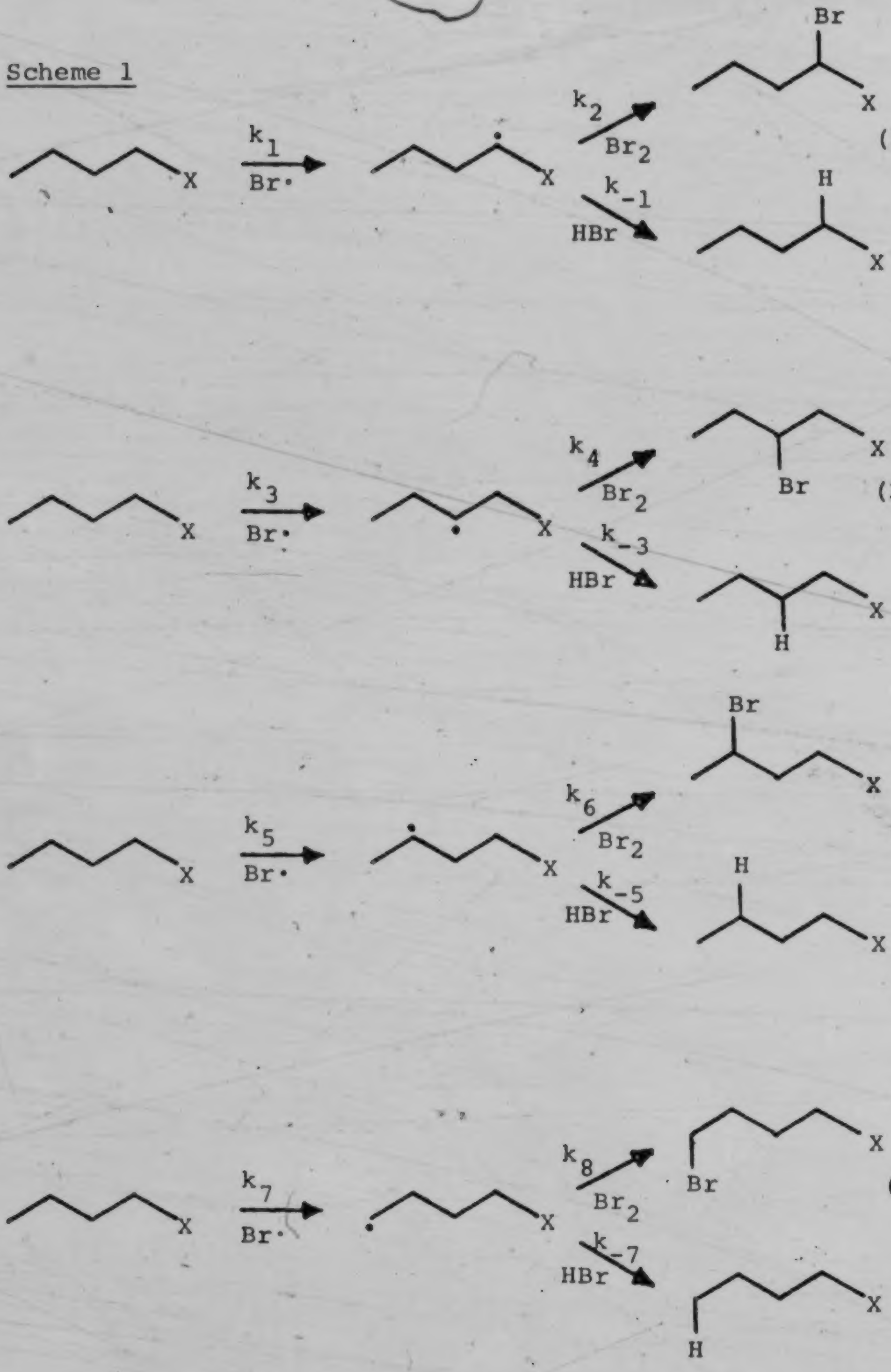
$$\frac{k_2}{k_{-1}} = \frac{[RBr][HBr]}{([RH]^f - [RH]^\circ)[Br_2]} \qquad (23)$$

The brominations of the perdeuterated substrates were therefore run to low conversion. The amount of brominated product was determined by glpc, while the amount of protiated substrate formed was determined by a comparison of the protium content after the reaction with that (residual protium) in the starting perdeuterated substrate (mass and/or nuclear magnetic resonance spectroscopy).

When a substrate has a number of positionally different deuteriums (e.g. 1-chlorobutane-d_9), this method will give the ratio of transfer with bromine and with hydrogen bromide for each position of the molecule, since the amount of product and protium incorporation at each position can be easily determined. For the comparison of any two positions in the same molecule (Scheme 1), the ratio of the rates of formation of products from these positions (e.g. the α- and γ-positions, see Scheme 1, reactions 25 and 26) is given by expression 24. Since the concentrations

$$\frac{d[R^\alpha Br]/dt}{d[R^\gamma Br]/dt} = \frac{k_1(k_{-5}/k_6 + [Br_2]/[HBr])}{k_5(k_{-1}/k_2 + [Br_2]/[HBr])} \qquad (24)$$

Scheme 1


k1
Br·
k2
Br2
Br
X
k-1
HBr
H
k3
k4
k-3
k5
k6
k-5
k7
k8
k-7

(25)

(26)

(27)

(28)

of bromine and hydrogen bromide do not change significantly during the reaction, equation 24 may be integrated; substituting for $k_{-1}[HBr]/k_2[Br_2]$ from equation 23, and for $k_{-5}[HBr]/k_6[Br_2]$ from a similar expression for the γ- position, the integrated form of expression 24 reduces to 29, which can easily be evaluated to give the value of the relative rates of abstraction of

$$\frac{k_1}{k_5} = \frac{[R^{\alpha}Br] + [R^{\alpha}H]^{f} - [R^{\alpha}H]^{\circ}}{[R^{\gamma}Br] + [R^{\gamma}H]^{f} - [R^{\gamma}H]^{\circ}} \qquad (29)$$

the α- and γ-hydrogens. Similar expressions may be written to give the relative rates of abstraction of the β- and γ-hydrogens, and the δ- and γ-hydrogens.

The values of the relative rates obtained by this method are those for the perdeuterated substrate: to apply these to the non-deuterated compound, it must be assumed that analogous ratios of rate constants for the compounds are the same, equation 30. For the ratios of

$$k_i^H/k_j^H = k_i^D/k_j^D \qquad (30)$$

the transfer rates with bromine and with hydrogen bromide, e.g. k_2/k_{-1} (Scheme 1), this assumption implies that the secondary deuterium kinetic isotope effects are the same for the two transfer reactions. This is not unreasonable, since both reactions are exothermic, and secondary isotope effects are usually small.[37,88,89] For the ratios of the rates of abstraction, e.g. k_1/k_5 (Scheme 1), equation 30 assumes that primary and secondary isotope effects in the abstraction of deuterium are the same at all positions in the molecule. This assumption may not hold, especially for the α-position, where the C-H bond strength may be affected by the substituent.

Fortunately, the relative rates of abstraction may be independently determined by carrying out the vapour phase bromination of the protiated substrate under conditions where the Br_2/HBr ratio is always much larger than unity, so that reaction 4 cannot compete with reaction 5 (pages 7,8). This may be done by carrying out the reaction to very low percent conversion of the bromine, or by using a large excess of bromine. Under these conditions the relative rate of abstraction of, e.g., the α- and γ-hydrogens (Scheme 1) is given by equation 31.[22] The results

$$\frac{k_1}{k_5} = \frac{[R^{\alpha}Br]}{[R^{\gamma}Br]} \qquad (31)$$

obtained by this method may then be compared with those obtained from the kinetics of the perdeuterated substrate to check the validity of equation 30.

A second test for the validity of the relative rates obtained and for the mechanism of bromination proposed in Scheme 1 is also available. In the bromination of a protiated substrate with a deficiency of bromine and no initially added hydrogen bromide ("normal" bromination), equation 24 gives the ratio of the rates of formation of two of the products. Since the ratio $[Br_2]/[HBr]$ is a monotonic function of time, using the substitution $[Br_2]/[HBr]=x$, the rate of formation of any product may be expressed in terms of x (equation 32), and equation 24 may

$$d[RBr]/dt = (d[RBr]/dx)(dx/dt) \tag{32}$$

be rewritten as equation 33. Similar expressions can be

$$\frac{d[R^{\alpha}Br]/dx}{d[R^{\gamma}Br]/dx} = \frac{k_1(k_{-5}/k_6 + x)}{k_5(k_{-1}/k_2 + x)} = f^{\alpha/\gamma} \tag{33}$$

written for the ratio of any two products. Expression 33 cannot be integrated for "normal" brominations, but by making use of the relative rates obtained from the bromination of the perdeuterated substrate, it may be evaluated for any value of x.

The ratio $f^{\alpha/\gamma}$ (equation 33) may also be determined experimentally. By determining the amount of products that are formed at different stages of the bromination of the protiated substrate under normal bromination conditions (i.e. at different values of x), plots of the concentration of each product against x may be constructed, and from the slope, the value of d[RBr]/dx may be determined for any value of x. The ratio of the experimentally determined slopes, $(d[R^{i}Br]/dx)/(d[R^{ii}Br]/dx)$, may then be compared with the value calculated from equation 33; the fit -- or lack of one -- between the two values will give an estimate of the reliability of the kinetic data obtained and their applicability to "normal" bromination reactions.

II.2 Cyclohexane

The photobromination of cyclohexane has been studied by a number of workers.[90-93] The reaction has a quantum yield of about 2 at room temperature, and 12-37 at 100°, and is strongly inhibited by oxygen.[93] The C-H bond dissociation energy for cyclohexane is reported as 94.9 kcal./mol,[94] and therefore the abstraction of hydrogen by bromine atoms from cyclohexane will be 7.4 kcal./mol endothermic (the H-Br bond dissociation energy is 87.5 kcal./mol[32]). The reversal reaction with hydrogen bromide will therefore be 7.4 kcal./mol exothermic, and is expected to compete well with transfer with bromine.

The relative rate of transfer of cyclohexyl radicals with bromine (k_2) and with hydrogen bromide (k_{-1}) was determined by running the photobromination of perdeuteriocyclohexane with excess bromine and excess hydrogen bromide in the vapour phase. As already noted, under these conditions, this reaction will not be complicated by any other effects.

II.2.1 Determination of k_2/k_{-1}

Perdeuteriocyclohexane (99.4 atom % D), bromine and hydrogen bromide were placed in a degassed reaction vessel (5 or 22 l), see Table 5. The reaction vessel was all Pyrex glass, and was isolated from the vacuum line by a high-vacuum teflon "Rotaflo" stopcock. After equilibration in the absence of light, the reaction mixture was photolyzed with incandescent light at ambient temperature until the perdeuteriocyclohexane had reacted to between 2-19%. The contents of the vessel were collected in the dark, and the residual bromine and hydrogen bromide were destroyed with aqueous sodium bisulphite. An aliquot of a Freon 113 solution of an internal standard, o-dichlorobenzene, was added, the organic material was extracted with Freon 113, dried, and analyzed by glpc for starting material and products. The

Table 5

Photobromination of Perdeuteriocyclohexane with Excess Bromine and Excess Hydrogen Bromide in the Vapour Phase

	Concentration M, x 10^5				
	1^a	2^a	3^a	4^b	5^b
Reactants[c]					
$[C_6(DH)_{12}]°$	22.4	25.5	25.2	109	110
$[Br_2]°$	35.6	38.8	37.7	155	176
$[HBr]°$	150	283	36.2	160	157
$[C_6D_{11}H]°$	1.41	1.46	1.58	6.87	6.92
Products[c]					
$[C_6(DH)_{12}]$	17.3	22.8	23.4	105	98.6
$[C_6D_{11}H]$	8.00	6.01	2.11	7.73	9.59
$[C_6D_{11}Br]$	2.94	1.50	1.48	2.32	7.60
$[C_6D_{10}Br_2]^d$	1.54	0.26	0.00	0.00	0.88
Temperature	24.0°	28.0°	20.0°	20.2°	22.2°
% Reaction[e]	18.9	7.2	5.9	2.1	7.9
k_2/k_{-1}[f]	2.74	2.88	2.72	2.80	2.89

[a] Run in 22 l reaction bulb.

[b] Run in 5 l reaction bulb.

[c] $[C_6(DH)_{12}]$ refers to the concentration of perdeuteriocyclohexane.

continued.....

Table 5 (cont'd.)

[d] Sum of 1,2- and 1,1-dibromoperdeuteriocyclohexane.

[e] Based on perdeuteriocyclohexane.

[f] Calculated using equation 23. The amount of brominated product was taken as the sum of the mono- and di-bromination products. The average values of $[Br_2]$ and [HBr] during the reactions were used; this correction was only significant when the conversion was greater than 10% (i.e. reaction 1).

material balance on the recovered organic material was always between 96 and 99%. The unbrominated perdeuteriocyclohexane was collected by preparative glpc and its protium content was compared, using mass and nuclear magnetic resonance spectroscopy, to that before reaction.

The isolated reaction mixture showed no detectable products other than perdeuteriocyclohexane and its mono- and di-bromination products (see Table 5). The bromination products had the same glpc retention times as bromocyclohexane, trans-1,2-dibromocyclohexane, and 1,1-dibromocyclohexane. The mass spectral cracking patterns of these products, isolated by preparative glpc, were identical with those of the authentic undeuterated compounds, when the m/e values were corrected for the presence of deuterium instead of protium.

Control experiments were performed on known mixtures of cyclohexane, bromocyclohexane, trans-1,2-dibromocyclohexane, bromine and hydrogen bromide. A mixture corresponding to the final product composition obtained in reaction 1, Table 5, was placed in the vapour phase (22 l reaction vessel), equilibrated in the absence of light for 1 hour, reisolated, and subjected to the analytical procedure. The material balance on carbon was 98.8%, while that based on the brominated compounds was

99.7%. The ratio of trans-1,2-dibromocyclohexane to bromocyclohexane was found to increase slightly (~2%); however, the material balance was found to be quantitative within the experimental limits quoted.

For the calculation of k_2/k_{-1} (equation 23), the amount of bromination product, RBr, had to be determined. Since the dibrominated material must have arisen, regardless of mechanism, from the monobrominated substitution products, the extent of monobromination was calculated as the sum of the mono- and di-brominated products. This assumption must indeed be correct, since reactions yielding dibromides (reactions 1, 2, and 5, Table 5) and reactions not yielding dibromides (reactions 3 and 4, Table 5) gave the same average relative rate constant, within experimental error.

The variation in the amount of 1,2- and 1,1-dibromocyclohexane obtained in these reactions does not appear to arise from a competition having a constant ratio of rates for the abstraction of hydrogen from cyclohexane and bromocyclohexane. The relative rate of bromination of bromocyclohexane and cyclohexane is known to depend on the concentration of hydrogen bromide in the reaction mixture (see Table 3), bromocyclohexane reacting faster than cyclohexane in the presence of hydrogen bromide.[44]

While this must be part of the reason for the variable amounts of dibromocyclohexanes formed, it does not account for the difference in the amounts of dibromides in reaction 5 and 4 or 3 (Table 5). It is possible that an ionic (dark) reaction was occuring in some instances between bromocyclohexane and bromine and hydrogen bromide[44] in the condensed phase, i.e. when the material was in the liquid phase prior to isolation. This is supported by the slight increase in the ratio of 1,2-dibromocyclohexane to bromocyclohexane in the control reaction described above. As discussed previously, the production of dibrominated products, irrespective of the mechanism, will not affect the relative rate data reported.

The relative rates of transfer of perdeuteriocyclohexyl radicals with bromine and with hydrogen bromide were calculated using equation 23; the average value was 2.81±0.06, and no dependence on the $[Br_2]/[HBr]$ ratio (from 1:0.9 to 1:7) was detected. The temperature at which the reactions were carried out varied from 20° - 28°; the difficulty in controlling the temperature of the large vessels used for the reactions was worrysome. However, our rates are relative rates, which should both increase with increasing temperature, and the average of five determinations did not deviate by more than ±2% over the 8° temperature range used. It seems therefore justified to assume that the value of the relative rates of transfer in these reactions is insensitive to temperature over this small temperature range.

The results show that 26% of the perdeuteriocyclohexyl radicals transfer with hydrogen bromide when the concentrations of hydrogen bromide and bromine are equal. The ratio k_2/k_{-1} is expected to be the same for perdeuteriocyclohexyl radicals and cyclohexyl radicals (see page 40); in the bromination of cyclohexane under "normal" bromination conditions, where the Br_2/HBr ratio is less than unity at more than 50% conversion of the bromine, a significant amount of the radicals will therefore regenerate starting material.

II.2.2 Comparison of Vapour and Liquid Phase Values of k_2/k_{-1}

The value of k_2/k_{-1} was determined in Freon 113 solution in these laboratories in a study parallel to this one.[95] Unlike the vapour phase result, k_2/k_{-1} was found to be variable and dependent on the relative concentrations of bromine and hydrogen bromide (Table 6); k_2/k_{-1} varied from 1.13 ($[Br_2]/[HBr] = 0.7$) to 0.31 ($[Br_2]/(HBr] = 25$), and was always smaller than the vapour phase value. The

Table 6

Relative Rates of Transfer for Perdeuteriocyclohexane in Freon 113 Solution (30.0 ± 0.1°)[a,b]

$[C_6D_{12}]°$	$[Br_2]°$	$[HBr]°$	$[Br_2]/[HBr]$	k_2/k_{-1}[c]
2.05	5.21	3.77	1.4	0.84
1.30	1.46	2.14	0.7	1.13
2.11	5.40	3.87	1.4	0.78
2.32	22.9	3.22	7.1	0.36
1.46	58.9	2.37	25	0.31

[a] Taken from ref. 95.

[b] All concentrations M x 10^2.

[c] Calculated from equation 23.

reversal reaction is thus more important in solution than in the vapour phase, and it dominates the solution phase reaction (up to 76% of the radicals reversing with hydrogen bromide) when the bromine concentration is much larger than the hydrogen bromide concentration (see Table 6).

The difference between the vapour phase and liquid phase results and the variability of the ratio k_2/k_{-1} in solution were intriguing. These may be due to solvent effects on the relative rates of transfer of perdeuteriocyclohexyl radicals in solution, these effects being more pronounced as the solvent polarity was increased by the increasing amounts of molecular bromine. This is not likely, however, since no solvent effects have been reported for brominations with molecular bromine.[6,18,21,22] Further, even if there were any, they are expected to cancel out in the ratio k_2/k_{-1} since both transfer reactions are bimolecular.[19] The transition state for these reactions should not show much difference in polarity either, since both reactions are exothermic and perdeuteriocyclohexyl radicals themselves have no appreciable dipole moment.

A possible major difference between reactions run in the vapour and in the liquid phases could be the occurance of cage reactions in the latter phase. However, perdeuteriobromocyclohexane and protiated perdeuteriocyclohexane were both formed from "free" perdeuteriocyclohexyl radicals, unless cage scavenging (by bromine and/or hydrogen bromide) was taking place. Since the concentration of hydrogen bromide was kept nearly constant in the liquid phase reactions (Table 6), cage scavenging, if important, should have been most pronounced in the reactions having the highest bromine concentrations. Cage scavenging by bromine would result in an apparently increased value of the rate constant k_2, and consequently would increase the calculated value of the ratio k_2/k_{-1}, rather than decrease it, as was actually observed.

If it is assumed that the relative rates of transfer with bromine and with hydrogen bromide in the vapour and liquid phase are the same, the lower value of the ratio in solution implies that transfer with a species other than hydrogen bromide was occurring at a faster rate than transfer with hydrogen bromide to produce protiated perdeuteriocyclohexane. The alternative explanation -- that the bromine concentration in solution was actually lower than thought -- was not considered likely, since it would require an unprecedented self-complexing of bromine,[56] with a very large equilibrium constant.

An attractive proposal to explain why perdeuteriocyclohexyl radicals reverse more in solution than in the gas phase is that the transfer agent in solution is a complex of hydrogen bromide and molecular bromine (reaction 34), and that the rate constant for this process, k'_{-1} reaction 35, is larger than that for transfer

$$HBr + Br_2 \longrightarrow HBr_3 \tag{34}$$

$$C_6D_{11}\cdot + HBr_3 \xrightarrow{k'_{-1}} C_6D_{11}H + Br_2 + Br\cdot \tag{35}$$

with hydrogen bromide. Complexes of the type HX_3 are well established for bromine,[61,62] chlorine[96] and iodine;[97,98] the equilibrium constant for the formation of the iodine complex has been reported to be between 25 - 400 l/mol (CCl_4, 25°),[97] and solid hydrogen tribromide was isolated by cooling solutions of bromine in hydrobromic acid.[62]

If equations 34 and 35 are included in the mechanism used to derive the relative rates of appearance of products (RBr and RH) in solution, expression 22 becomes equation 36. Integration of 36 and rearrangement gives 37. This expression may be evaluated to give the

$$\frac{d[RBr]/dt}{d[RH]/dt} = \frac{k_2([Br_2]° - [HBr_3])}{k_{-1}([HBr]° - [HBr_3]) + k'_{-1}[HBr_3]} \tag{36}$$

$$\frac{[RBr]}{\Delta[RH]} \cdot \frac{k_{-1}}{k_2} = \frac{[Br_2]° - [HBr_3]}{[HBr]° - [HBr_3] + [HBr_3]k'_{-1}/k_{-1}} \tag{37}$$

ratio k'_{-1}/k_{-1}, the relative rate of transfer of perdeuteriocyclohexyl radicals with hydrogen tribromide and hydrogen bromide, using the vapour phase value for k_2/k_{-1} if the concentration of hydrogen tribromide was known. A study of Freon 113 solutions of bromine and hydrogen bromide was therefore undertaken.

Solutions of hydrogen bromide in Freon 113 with and without added molecular bromine were studied by uv and ir spectroscopy: no bromine induced shift could be observed in the ir spectrum of hydrogen bromide, and hydrogen bromide produced no shift in the position of the bromine absorption in the visible spectrum. The solutions were therefore studied by nuclear magnetic resonance spectroscopy.

II.2.3 NMR Method for Determining Complex Formation

Association between two molecules (e.g. reaction 34) can be readily studied by nmr spectroscopy in two limiting cases. In the case of slow exchange of the proton between the two molecules, separate signals will be observed for HBr and HBr_3, and their concentration may be evaluated independently. When rapid exchange takes place, only a single, population-weighted average shielding will be observed, the position of which, δ, is given by equation 38, where n_1 and n_2 are the mole fractions of

$$\delta = \delta_1 n_1 + \delta_2 n_2 \tag{38}$$

of HBr and HBr_3 respectively, and δ_1 and δ_2 are the positions of the signals of the proton in HBr and HBr_3.[99] To observe both associated and unassociated states in an equilibrium of the form of equation 34, the lifetime of each state must be longer than the reciprocal of the difference in chemical shift (expressed in frequency units) between HBr and HBr_3. For a typical difference of 500 Hz, lifetimes greater than 10^{-3} second would be required to observe separate signals for the two species. As the lifetimes become shorter, the increased exchange rate results in a broadening of the separate signals which coalesce into the single peak given by equation 38 when the lifetime reaches the value $\sqrt{2}/2\pi\Delta$, where Δ is the separation of the two signals in Hz in the absence of exchange.[100]

II.2.4 NMR Study of Freon 113 Solutions of HBr and Br_2

The hydrogen bromide proton was found to absorb at 356.2 ± 0.4 Hz above TMS in Freon 113 at 32.8°, and at 355.4 ± 0.8 at 23° (100 MHz proton nmr spectrum). The solubility of hydrogen bromide in Freon 113 is unfortunately rather low,[103] and therefore the position of absorption could only be studied over a small range of concentrations (Table 7). No concentration dependence was evident: this appears to negate the occurrance of self-association of hydrogen bromide in Freon 113, in agreement with the report of Martin and Fujiwara that no self-association of hydrogen bromide takes place in dichloromethane or in 1,1,2,2-tetrachloroethane.[102]

A pronounced temperature dependence of the shielding of the hydrogen bromide proton was observed (Table 8). The data gave a straight line plot (Figure 1), and shows a temperature dependence of 0.194 Hz/°C (equation 39). This dependence is intermediate between the

$$\delta = 0.194T + 350.1 \ (r = 0.999) \tag{39}$$

value reported in the gas phase (0.013 Hz/°C)[101] and in dichloromethane solution (0.447 Hz/°C).[102]

Solutions of hydrogen bromide in Freon 113 with added molecular bromine showed a downfield shift, the magnitude of which depended on the bromine concentration (Table 9), in aggreement with the idea of a complex formation between the two. The shift was 27.8 Hz when the solution was 3 M in bromine. To ascertain that the shift was due to complex formation, and not a solvent shift due to added bromine, the bromine induced shift of the shielding

Table 7

Concentration Dependence of the Hydrogen Bromide Proton Absorption in Freon 113[a]

[HBr], M	δ^b, 32.8°	δ^b, 23.0°
0.0205	357.0	
0.0509	357.0	357.3
0.0681	355.9	354.5
0.0764	355.7	355.4
0.0814	356.5	354.7
0.0925	355.3	355.1
0.0955[c]	356.1	
0.0963	356.0	
0.0981	356.4	
0.1510[d]	357.7	

---

[a] TMS internal standard; all spectra run on a Varian HA 100 spectrometer.

[b] Reported in Hz upfield from TMS; the average value was 356.2 ± 0.4 Hz at 32.8° and 355.4 ± 0.8 Hz at 23.0°.

[c] The solution was 0.1 M in cyclohexane.

continued.....

Table 7 (cont'd.)

[d] The reported concentration is calculated from the amount of hydrogen bromide added; probably not all the hydrogen bromide was in solution, since the solubility of hydrogen bromide in Freon 113 at 30° is ~0.1 M. This value was not used in the calculation of the average value of the absorption quoted in footnote b.

Table 8

Temperature Dependence of the Hydrogen Bromide Proton Absorption[a]

Temperature, °C	δ[b]
30.5	356.0
25.0	354.7
20.0	354.0
15.0	353.0
10.0	352.3
0.0	350.5
-10.0	348.2
-20.0	346.2
-30.0	344.1

[a] 0.102 M hydrogen bromide in Freon 113, 1% in TMS.

[b] Measured on a Varian HA 100 spectrometer, Hz upfield from TMS.

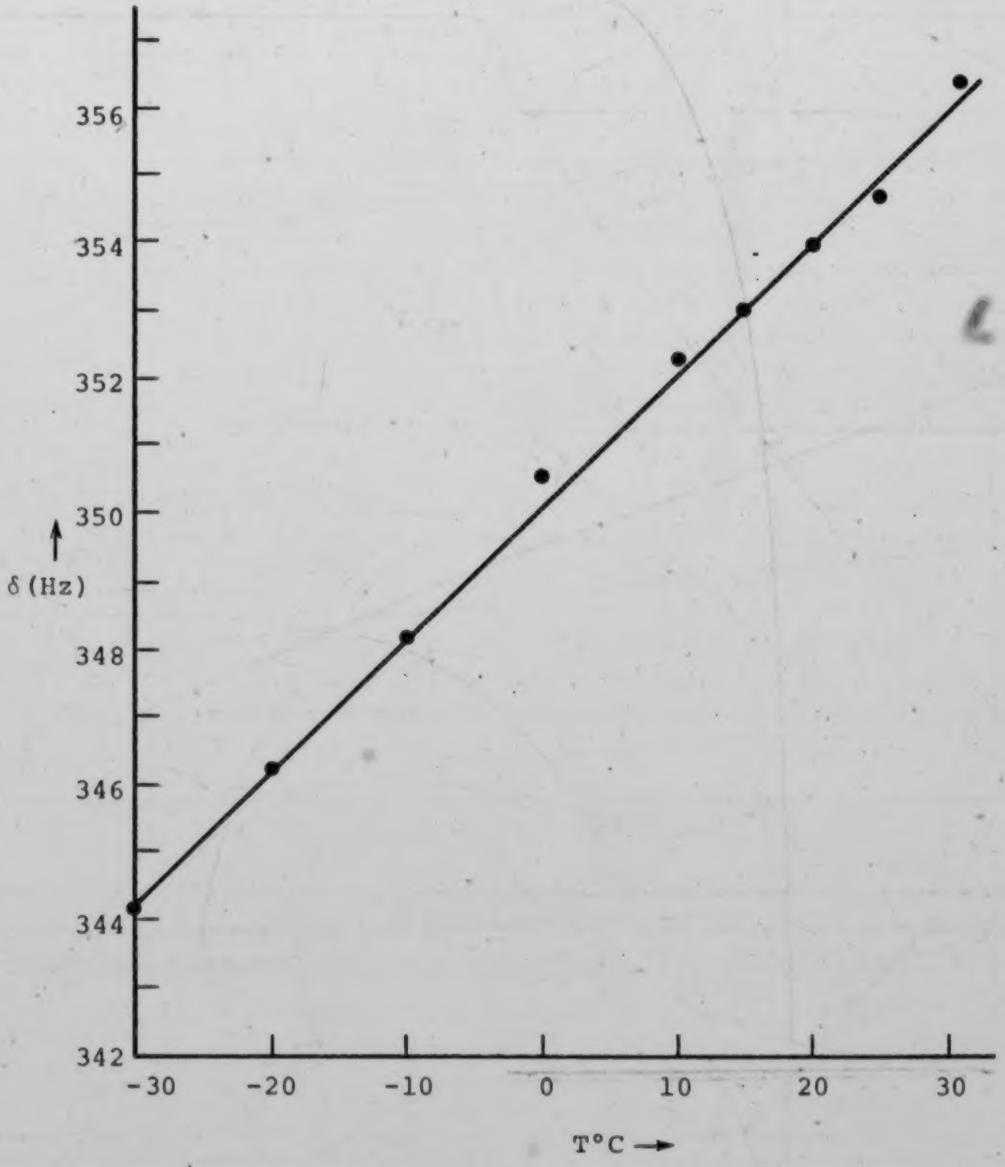


Fig. 1. Temperature Dependence of the Hydrogen Bromide NMR Absorption (100 MHz, Freon 113, TMS internal reference)

Table 9

Determination of the Equilibrium Constant for the Formation of HBr_3 by NMR[a]

$[HBr]°$, M	$[Br_2]°$, M	δ^b, 32.8°	δ^b, 23°	$K_{32.8°}$	$K^c_{32.8°}$	$K_{23°}$
0.0716	0.0153	354.9		3.5	3.6	
0.0675	0.0311	354.3	353.6	2.4	2.3	2.4
0.0475	0.0331	354.1		2.4	3.2	
0.0727	0.0310	353.8		3.3	2.6	
0.0338	0.0498	352.8		2.6	2.6	
0.0253	0.0600	352.1		2.7	3.1	
0.0793	0.0657	351.6		3.2	2.9	
0.0746	0.1372	348.0		3.0	2.9	
0.0723	0.1372	347.9		3.1	3.0	
0.0742	0.1860	345.6		3.1	3.0	
0.0655	0.1899	345.5	344.1	3.2	3.0	3.7
0.0630	0.3098	341.9	341.4	3.0	2.8±0.3 ave, $\Delta_c = 32.2^d$	3.1
0.0797	0.3563	341.7		2.7		

continued.....

Table 9 (cont'd.)

$[HBr]°$, M	$[Br_2]°$, M	δ^b, 32.8°	δ^b, 23°	$K_{32.8°}$	$K^c_{32.8°}$	$K_{23°}$
0.0594	0.5091	339.1	338.8	2.5		2.6
0.0715	0.5730	337.4		2.8		
0.0900	0.7328	335.7		2.8		
0.0651	1.040	333.5	333.8	2.7		2.6
0.0676	1.067	333.2		2.7		
0.0856	1.460	331.6		2.7		
0.0610	1.967	330.6		2.4		
0.0638	2.123	329.9	329.8	2.6		2.7
0.0750	2.994	328.7		2.5		2.8±0.3 ave, $\Delta_c = 29.9^d$
0.0998	2.948	328.4		2.8		
				2.8±0.3 ave, $\Delta_c = 31.3^d$		

continued.....

Table 9 (cont'd.)

[a] Freon 113 solvent.

[b] Reported in Hz upfield from TMS.

[c] Equilibrium constant at 32.8° determined from the data of the first eleven spectra only.

[d] Computed shift of HBr_3 signal relative to that of HBr.

of 2,2-dimethylpropane in Freon 113 was studied (Table 10). A small downfield shift was observed, up to 0.5 Hz in 3 M bromine solution. The results in Table 9 gave a straight line plot (equation 40). Since the shift was within the

$$\delta = 93.2 - 0.174[Br_2] \qquad (r = 0.998) \tag{40}$$

experimental error in the position of the hydrogen bromide absorption, any "solvent" shift could be neglected.

Figure 2 shows the effect of added bromine on the shielding of the hydrogen bromide proton in Freon 113 at 32.8 ± 0.2° and 23.0 ± 0.2°. The curve is smooth and approaches an asymptotic value as the bromine concentration increases, as expected for the formation of a complex between hydrogen bromide and bromine (equation 41).

$$K = [HBr_3]/([Br_2]^\circ - [HBr_3])([HBr]^\circ - [HBr_3]) \tag{41}$$

The value of the equilibrium constant K could not be determined directly since the concentration of "free" bromine in the solutions was not known initially. Two methods were used to get the value of K. In the first method,[95] the maximum shift observed (27.8 Hz) was assumed to be that of hydrogen tribromide; using this value for δ_2 in equation 38, a set of values for the equilibrium constant were determined (equation 34). From the average of these

Table 10

Bromine Induced Shift of the Shielding of 2,2-Dimethlpropane[a]

$[C_5H_{12}]$, M	$[Br_2]$	δ[b]
0.0795	0.00	93.2
0.0781	0.1188	93.2
0.0779	1.088	93.0
0.0781	2.936	92.7

[a] In Freon 113 at 32.8°. 100 MHz spectra.

[b] Hz downfield from TMS (internal standard).

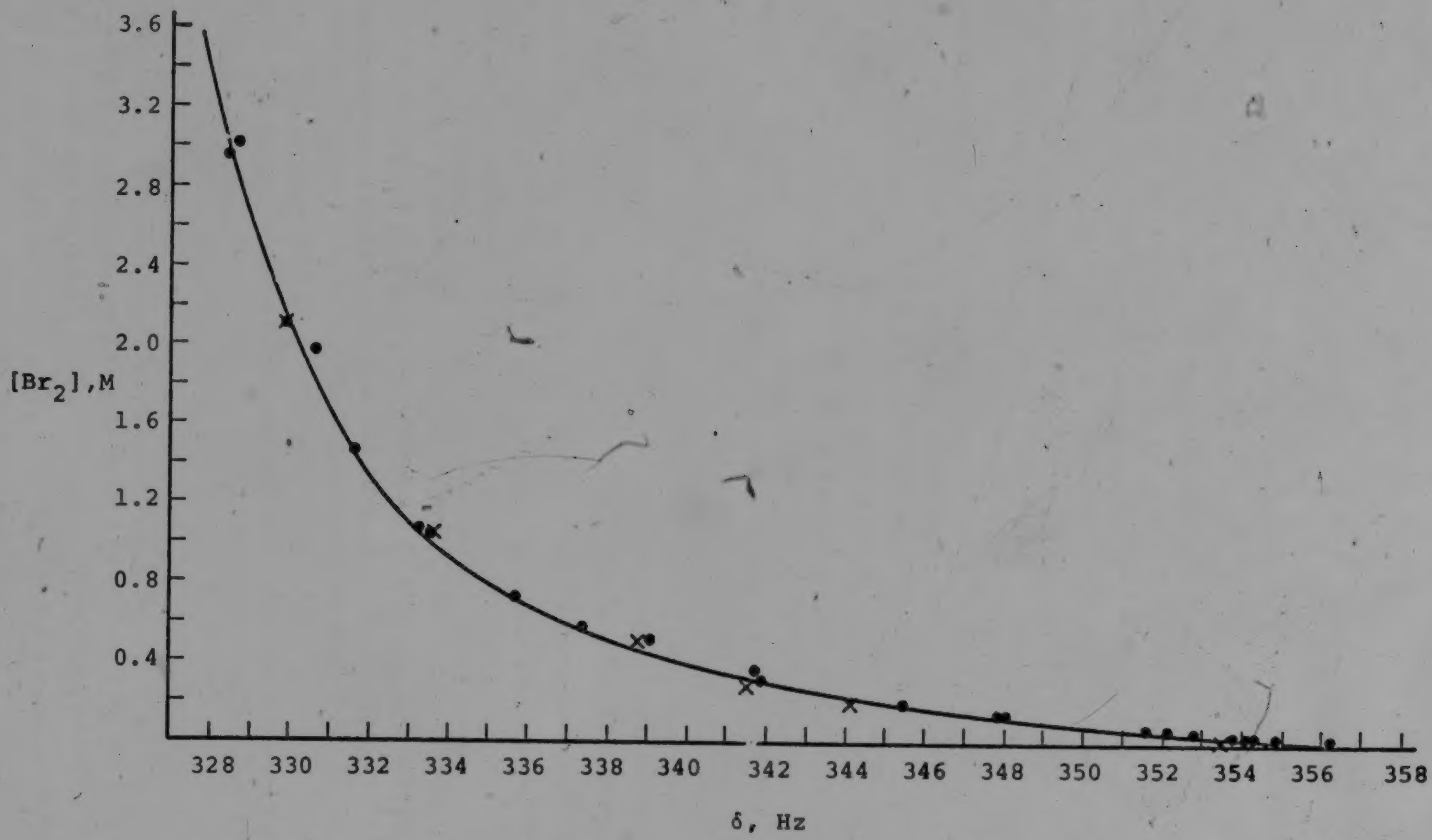


Fig. 2. Bromine Induced Shift of the 100 MHz NMR Absorption of Hydrogen Bromide (Freon 113, TMS internal reference; ● at 32.8°, x at 23.0°)

values, the amount of hydrogen tribromide in the solution with the maximum shift was calculated, and this used to give a new value for δ_2. The new value of δ_2 was used to calculate a new set of values for K, and the process was repeated until a constant average value of K was obtained (see Table 9). This method gave an average value of K of 2.8 ± 0.3, and the position of the hydrogen tribromide shielding was 324.9 Hz above TMS at 32.8°; the corresponding values at 23° were 2.8 ± 0.3, and 325.4 Hz above TMS.

In the second method, the Bernesi-Hildebrand-Scott (BHS) equation (equation 42) was used to calculate the shielding of the complex and the value of the equilibrium constant.[104,105]. In the BHS equation, Δ is the shift of

$$\frac{[Br_2]}{\Delta} = \frac{[Br_2]}{\Delta_c} + \frac{1}{K\Delta_c} \qquad (42)$$

the observed absorption of a solution containing bromine and hydrogen bromide from that of hydrogen bromide, $\Delta_c = \delta_{HBr} - \delta_{HBr_3}$. Again, an iterative procedure was used. Initially the total bromine concentration, $[Br_2]°$ (Table 9), was used to approximate the concentration of the free bromine, $[Br_2]$, and the value of Δ_c, determined from a least squares fit to the BHS equation, can be used to arrive at a better estimate of $[Br_2]$, since $[Br_2]$ is given by equation 43. These

$$[Br_2] = [Br_2]^\circ - (\Delta/\Delta_c)[HBr]^\circ \qquad (43)$$

values of $[Br_2]$ can be used for a second BHS analysis, yielding better values of Δ_c, and so on to self consistency. The BHS analysis gave a value for K of 3.0 ± 0.2, and the hydrogen tribromide shielding was 325.5 Hz above TMS at 32.8°, while at 23° K = 2.8 ± 0.3 and the hydrogen tribromide shielding was 325.5 Hz above TMS.

These results show that complex formation takes place between bromine and hydrogen bromide in Freon 113 solution. However, inherent in the nmr method for the calculation of the maximum shift by either method is the assumption that the chemical shift of complexes of higher order in bromine than HBr_3 (equation 44) have

$$HBr_3 + Br_2 \longrightarrow HBr_5 \xrightarrow{Br_2} HBr_7 \xrightarrow{Br_2} \text{etc.} \qquad (44)$$

approximately the same chemical shift as HBr_3, since it has been proposed that in aqueous solution complexes of the type HBr_5 and HBr_7 are formed at high $[Br_2]/[HBr]$ ratios.[61,62] This seems to be a valid assumption since when the value of K was computed (by the first method) by iterative treatment of the data, using only the solutions whose $[Br_2]/[HBr]$ ratio was less than five (see Table 9), the calculated value of K at 32.8° was 2.8 ± 0.3, and the shielding of hydrogen tribromide was 324.0 Hz above TMS, in very good agreement with the values determined using all the data in Table 9.

II.2.5 Transfer with Hydrogen Tribromide in Solution

Using the value of the equilibrium constant determined by nmr, the concentrations of hydrogen tribromide in the liquid phase photobrominations of perdeuteriocyclohexane with excess bromine and excess hydrogen bromide (Table 6) could be determined. Assuming that the rate of transfer of perdeuteriocyclohexyl radicals with bromine relative to that of transfer with hydrogen bromide, k_2/k_{-1}, was not significantly effected by solvent effects, equation 37 was used to determine the value of the relative rate of transfer of these radicals with hydrogen tribromide and with hydrogen bromide, k'_{-1}/k_{-1}. The average value of this ratio was found to be 21.8 ± 6.7; this calculation further assumed that at high ratios of bromine to hydrogen bromide, the rates of transfer with complexes of the type HBr_3, HBr_5, HBr_7 are quite similar (if higher complexes are important).

By combining the vapour phase value for k_2/k_{-1} and the calculated value for k'_{-1}/k_{-1} (equation 45), the relative rate of transfer of perdeuteriocyclohexyl radicals with bromine and with hydrogen tribromide can be calculated

$$k_2/k'_{-1} = (k_2/k_{-1})^{vp}/(k'_{-1}/k_{-1}) \qquad (45)$$

as 0.13 ± 0.04, i.e. reversal with hydrogen tribromide is favoured over transfer with bromine by a factor of 8. This accounts for the variability of the value of k_2/k_{-1} in solution calculated from expression 23, since increasing the bromine concentration necessarily increases the concentration of hydrogen tribromide and makes reversal more important.

These results show that reversal in liquid phase bromination reactions will be even more important than expected, and will always occur to larger extents than in the vapour phase, where the low concentrations normally used make complex formation unimportant. It would therefore appear that the lower ratio of k_2/k_{-1} in solution compared to the vapour phase value is fundamental to brominations in solution.

II.2.6 Cage Effect in the Bromination of Cyclohexane and Perdeuteriocyclohexane

Under the conditions used for the bromination of perdeuteriocyclohexane, the presence of a cage reaction could not be detected since in solution, the ratio of products (RBr and RH) depends on the "free" perdeuteriocyclohexyl radicals. One way cage return may be studied is in competitive brominations (inter- or intramolecular), where cage filtering will produce a change in the relative reactivities in solution compared to the vapour phase (cf. section I.2.2). A study of the relative rates of bromination of cyclohexane and of perdeuteriocyclohexane was therefore undertaken.

Under conditions were no external reversal takes place, if cage reversal is important, two mechanisms can be formulated for the gas and liquid phase brominations, Schemes 2 and 3 respectively. The rate of disappearance of cyclohexane relative to that of perdeuteriocyclohexane from Scheme 2 is given by equation 46, which may be

$$\frac{d[C_6H_{12}]/dt}{d[C_6D_{12}]/dt} = \frac{k_1^H[C_6H_{12}]}{k_1^D[C_6D_{12}]} \qquad (46)$$

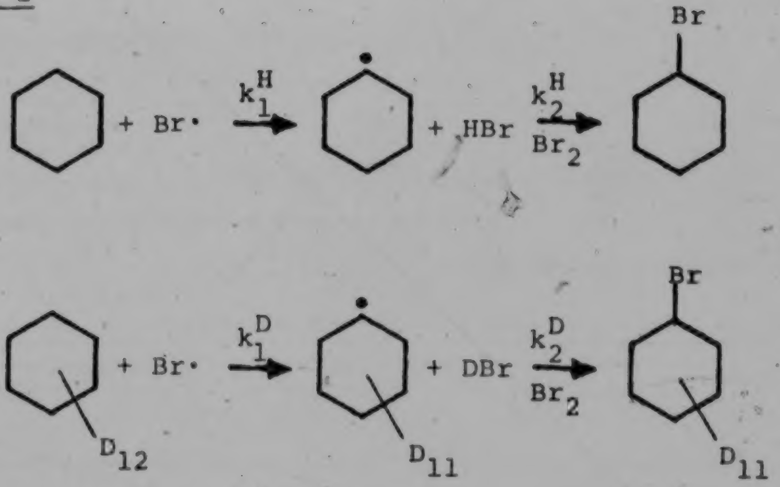
integrated to give the ratio k_1^H/k_1^D (equation 47). For the

$$k_1^H/k_1^D = \ln([C_6H_{12}]°/[C_6H_{12}])/\ln([C_6D_{12}]°/[C_6D_{12}]) \qquad (47)$$

solution case, Scheme 3, the corresponding two equations are 48 and 53, where $[HBr]^c$ and $[DBr]^c$ are the cage concentrations of hydrogen and deuterium bromide respectively.

$$\frac{d[C_6H_{12}]/dt}{d[C_6D_{12}]/dt} = \frac{k_1^H(k_{-1}^D[DBr]^c + k_d^D)}{k_1^D(k_{-1}^H[HBr]^c + k_d^H)} \qquad (48)$$

Scheme 2

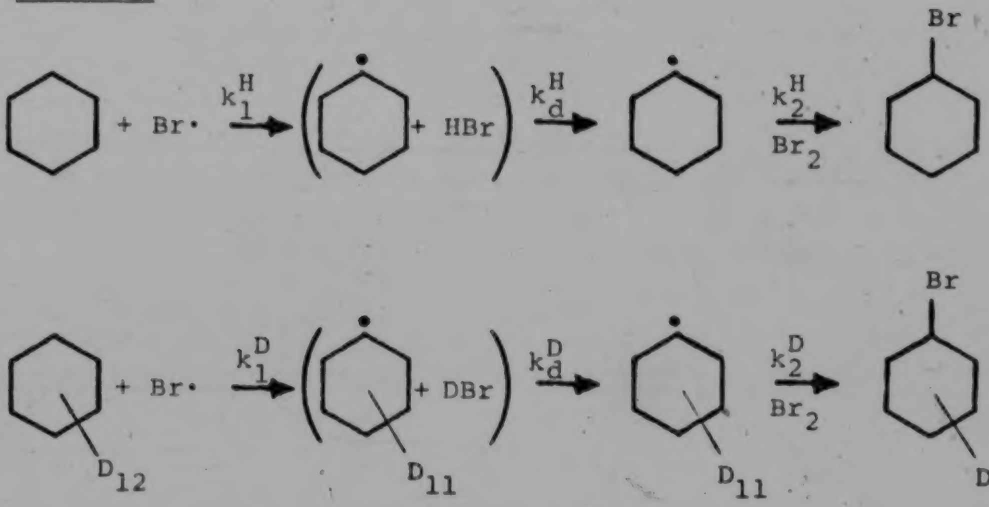


+ Br·
k_1^H
+ HBr
k_2^H
Br_2
Br
+ Br·
k_1^D
+ DBr
k_2^D
Br_2
Br
D_{12}
D_{11}
D_{11}

(49)

(50)

Scheme 3



+ Br·
k_1^H
+ HBr
k_d^H
k_2^H
Br_2
Br
+ Br·
k_1^D
+ DBr
k_d^D
k_2^D
Br_2
Br
D_{12}
D_{11}
D_{11}
D_{11}

(51)

(52)

$$(k_1^H/k_1^D)^{sol} = \frac{\ln([C_6H_{12}]^\circ/[C_6H_{12}])}{\ln([C_6D_{12}]^\circ/[C_6D_{12}])} = \frac{k_1^H(k_{-1}^D[DBr]^c + k_d^D)}{k_1^D(k_{-1}^H[HBr]^c + k_d^H)} \quad (53)$$

Since the rate of diffusion may be assumed to be proportional to the inverse square root of the molecular weight,[106] k_d^H and k_d^D are very nearly the same, and equation 53 may be rewritten as equation 54. This equation predicts

$$C_D^H = \frac{(k_{-1}^H[HBr]^c + k_d)}{(k_{-1}^D[DBr]^c + k_d)} = \frac{k_1^H}{k_1^D} \cdot \frac{1}{(k_1^H/k_1^D)^{sol}} \quad (54)$$

that the rate of bromination of cyclohexane relative to that of perdeuteriocyclohexane in solution in the absence of external reversal will be smaller than the relative rate in the vapour phase, since k_{-1}^H is bigger than k_{-1}^D. Also, if there are negligible solvent effects on the relative rates of abstraction, the cage effect, C_D^H defined as $(k_{-1}^H[HBr]^c + k_d)/(k_{-1}^D[DBr]^c + k_d)$, may be determined from a comparison of the vapour and liquid phase results (equation 54).

The relative rate of bromination of cyclohexane to that of perdeuteriocyclohexane was determined in the vapour phase using a sufficiently high concentration of bromine so that reversal of the radicals formed would not compete with transfer with bromine. The reactants and Freon 112 (internal standard) were introduced into a 5 l reaction bulb, equilibriated in the dark, and then photolyzed until at least 12% of the perdeuteriocyclohexane had reacted. The contents of the bulb were collected, the excess bromine destroyed, and the organic material extracted with Freon 113, the solution dried and then analyzed by glpc to determine the amount of reaction of each substrate (Table 11). Mass spectral analysis of the unbrominated substrates before and after the reaction confirmed the absence of reversal (Table 12). Since abstraction of deuterium from perdeuteriocyclohexane involves contributions from both α and β secondary deuterium isotope effects, the intermolecular isotope effect (k_H/k_D) cannot be determined, and although these effects are small,[37,88,89] the values obtained are reported as k_{RH}/k_{RD} and not k_H/k_D (Table 11).

The relative rate of bromination was calculated from equation 47, and was found to be 5.4 ± 0.1, and the ratio was independent of the concentration of bromine used. This value is much larger than the isotope effect of 2.4 (80°) reported by Urry for cyclohexane-d_1, which was obtained in solution and probably under reversible conditions.[36] The value k_{RH}/k_{RD} was also studied in these

Table 11

Competitive Photobromination of Cyclohexane and Perdeuteriocyclohexane in the Vapour Phase[a]

Reaction #	Concentration, M x 10^5					k_{RH}/k_{RD}[b]
	$[C_6H_{12}]^\circ$	$[C_6D_{12}]^\circ$	$[Br_2]^\circ$	$[C_6H_{12}]$	$[C_6D_{12}]$	
1	5.25	5.10	41.1	0.560	3.30	5.14
2	5.25	5.10	41.1	1.35	3.98	5.48
3	5.25	5.10	41.1	1.20	3.88	5.40
4	5.25	5.10	80.8	2.26	4.38	5.54
5	5.25	5.10	81.3	0.985	3.73	5.35

[a] All reactions were run in a 5 l reaction vessel at 21°.

[b] Calculated using equation 47; the average was 5.38 ± 0.11.

Table 12

Isotopic Composition of the Parent Ions from Cyclohexane and Perdeuteriocyclohexane Before and After Bromination[a]

Reaction #	M^+, %				M^+, %			
	d_{12}	d_{11}	d_{10}	d_9-d_0	d_{12}-d_3	d_2	d_1	d_0
	94.0	6.0	0.0	0.0	0.0	0.0	0.0	100.0
	93.7	6.0	0.3	0.0	0.0	0.0	0.0	100.0
	93.7	6.3	0.0	0.0	0.0	0.0	0.0	100.0
1	93.8	6.0	0.2	0.0	0.0	0.0	0.0	100.0
2	94.0	5.8	0.2	0.0	0.0	0.0	0.0	100.0
4	93.9	6.1	0.0	0.0	0.0	0.0	0.0	100.0

[a] Run on an AEI MS9 mass spectrometer at 10-12 ev; values reported are corrected for C^{13} natural abundance.

laboratories in Freon 113 solution under various conditions (Table 13).[55] The ratio was found to depend on the concentration of bromine used. Under "normal" bromination conditions (first two reactions in Table 13), k_{RH}/k_{RD} was 3.1 (21°). Mass spectroscopy showed that extensive reversal has occurred, and therefore this low result was due to both external and internal reversal.

As the concentration of bromine was increased, so that the ratio of bromine to hydrogen bromide increased, the amount of external scrambling was reduced, and above 0.07 M bromine, when the ratio $[Br_2]/[HBr]$ was always greater than 15, external reversal was eliminated (Table 13), and k_{RH}/k_{RD} was found to be 4.3 ± 0.1. The difference between 5.4, the vapour phase result, and 4.3 was attributed to cage reversal. From equation 54, the cage effect C_D^H, is found to be 0.80, showing that cage filtering of the cyclohexyl radicals takes place to a higher extent than that for perdeuteriocyclohexyl radicals, as expected.

When the concentration of bromine was increased to 7.7 M, it was anticipated that the observed value of k_{RH}/k_{RD} would increase due to cage scavenging of the radicals by the high concentration of molecular bromine.

Table 13

Competitive Photobromination of Cyclohexane and Perdeuteriocyclohexane in Freon 113[a,b]

$[C_6H_{12}]^\circ$	$[C_6D_{12}]^\circ$	$[Br_2]^\circ$	External Reversal[c]	k_{RH}/k_{RD}[d]	Average k_{RH}/k_{RD}
732	726	652	Observed[e]	3.10	3.12 ± 0.02
732	726	652	Observed[e]	3.13	
4.96	5.04	33.6	Observed[f]	3.65	
4.75	4.83	68.6	None	4.73	4.52 ± 0.21
4.75	4.83	68.6	None	4.31	
5.61	5.71	103	--	4.36	4.21 ± 0.16
5.61	5.71	103	--	4.05	
4.91	4.99	149	None	4.19	4.34 ± 0.14
4.91	4.99	149	None	4.48	
4.79	4.87	1030	--	4.15	4.14 ± 0.02
4.79	4.87	1030	None	4.12	
23.2	22.8	3630	--	4.22	4.32 ± 0.10
23.2	22.8	3630	--	4.42	
23.2	22.8	7710	--	4.42	4.67 ± 0.17
23.2	22.8	7710	--	4.50	
23.2	22.8	7710	--	4.77	

continued.....

Table 13 (cont'd.)

$[C_6H_{12}]^\circ$	$[C_6D_{12}]^\circ$	$[Br_2]^\circ$	External Reversal[c]	k_{RH}/k_{RD}[d]	Average k_{RH}/k_{RD}
23.2	22.8	7710	--	4.79	
23.2	22.8	7710	--	4.86	
23.2	22.8	10200	--	5.05[g]	5.34 ± 0.25
23.2	22.8	10200	--	5.49[g]	
23.2	22.8	10200	--	5.69[g]	
23.2	22.8	10200	--	5.11[g]	
180	190	18300	--	5.07[g]	5.33 ± 0.20
180	190	18300	None	5.72[g]	
186	190	18200	--	5.30[g]	
186	190	18200	--	5.23[g]	

---

[a] Taken from ref. 55. All reactions were run at 21°.

[b] Concentrations M x 10^3.

[c] Reactions with blank entries were not checked by mass spectrometry.

[d] Calculated from Equation 47.

[e] Approximately 10% incorporation observed.

[f] Approximately 0.3% incorporation observed.

[g] Run in liquid bromine solvent.

In their study of the competitive rates of bromination of alkanes and substituted alkanes, Tanner *et al.*[44] found that the rate of bromination of electronegatively substituted alkanes decreased relative to that of the parent alkanes as the bromine concentration increased, see Table 3. This was attributed to the supression of both internal and external reversal with hydrogen bromide at the high bromine concentrations.

As the concentration of bromine in the solution competitive brominations was increased further, k_{RH}/k_{RD} increased, showing that not only was external reversal eliminated, but scavenging from the cage becomes observable. When liquid bromine was used for the brominations ($[Br_2] > 10$ M), cage return was essentially stopped and the value for the observed k_{RH}/k_{RD} was found to be the same as in the vapour phase (5.4 ± 0.1 in the vapour phase, and 5.3 ± 0.2 in liquid bromine).

In the classic studies by Hammond on the effect of cage recombination on the yield of "free" radicals obtained from the decomposition of azo-bis-*iso*-butyronitrile (AIBN), it was found that molecular bromine could act as an effective scavenger of radicals free of the solvent cage. It was further reported that when the AIBN decomposition was carried out in liquid bromine, cage recombination was completely eliminated by scavenging of the radicals from the solvent cage.[107]

The coincidence of the k_{RH}/k_{RD} value in liquid bromine with that in the vapour phase gives strong evidence to the mechanisms proposed in Schemes 2 and 3, and makes it improbable that the effect is a solvent effect. Though it seems unlikely that there are no solvent effects on the individual rates on changing the solvent from the inert Freon 113 to the very polar bromine, it is reasonable that the effects will be the same on k_1^H and k_1^D, and consequently will cancel out in the ratio k_{RH}/k_{RD}.

The mechanisms proposed in Schemes 2 and 3 may be used to rationalize the previously puzzling anomaly pointed out by Timmons.[108] The intramolecular primary deuterium isotope effect for the photobromination of toluene-α-d_1 has been carefully studied in the solution[37] and vapour phase.[108] Both groups were careful to exclude observable reversal reaction (i.e. reactions in solution corresponding to reactions of radicals free of the solvent cage). The solution phase isotope effect was found to be 4.59 ± 0.03 (CCl_4, 77°), while the value obtained in the vapour phase was calculated (equation 55) to be 8.2 at 77°.

$$k_H/k_D = (1.08 \pm 0.25)\exp(1430 \pm 110)/RT \qquad (55)$$

The difference is probably due to cage filtering in solution, and the calculated cage effect (equation 54) for the bromination of toluene-α-d_1 is 0.56. Cage filtering would be expected to be more important for the near thermoneutral transfer reactions of the more stable, more selective benzyl radicals, than for the exothermic, less selective transfer of cyclohexyl radicals with hydrogen bromide.

It is relevant to note that in the study of the solution and gas phase isotope effect for the chlorination of deuterated toluene, where reversal is energetically unfavourable (E_a>18 kcal/mol), Walling and Miller found that the value of k_H/k_D was independent of phase.[25]

II.3 1-Chlorobutane

The bromination of perdeuterio-1-chlorobutane was investigated to determine the effect of the electronegative substituent on the molecule as a whole and in particular on the different positions of the molecule. The reaction of 1-chlorobutane with molecular bromine in the vapour phase at 100° was reported by Kharasch, Zimmt and Nudenberg to give three products: 1-bromo-1-chlorobutane (23%), 2-bromo-1-chlorobutane (23%), and 3-bromo-1-chlorobutane (46%).[109]

Very similar results were obtained by Fredricks and Tedder,[13] who carried out the reaction in a fast-flow reactor at 146°. The liquid phase reaction also gave very similar results (neat 1-chlorobutane, 60°, 1-bromo-1-chlorobutane, 23%, 2-bromo-2-chlorobutane, 25% and 3-bromo-1-chlorobutane, 52%).[66] These results are expected on the basis of polar effects on the transition state for hydrogen abstraction at the different positions along the molecule. No 1,2-dibromobutane has been reported in these brominations, showing that β-chlorobutyl radicals do not eliminate chlorine atoms to give alkene under these conditions.

All these results were obtained under "normal" bromination conditions, and the product distribution was probably influenced by reversal. A study of the kinetics of the vapour phase photobromination of perdeuterio-1-chlorobutane was therefore undertaken to determine the relative rates of transfer of the isomeric chlorobutyl radicals with bromine and with hydrogen bromide (Scheme 1, X=Cl). If it is assumed that the rate of transfer with bromine is the same for the different chlorobutyl radicals, a comparison of the relative rates of transfer with bromine and with hydrogen bromide would give an estimate of the polar effect of the chlorine substituent on the transfer reaction with hydrogen bromide at the different positions of the molecule. This assumption is not unreasonable since polar interactions should be negligible for transfer of a polar molecule with a non-polar bromine molecule.

II.3.1 Kinetics of Bromination of Perdeuterio-1-chlorobutane

The vapour phase photobromination of perdeuterio-1-chlorobutane with excess bromine and excess hydrogen bromide in a 22 l reaction vessel was carried out using the method described for perdeuteriocyclohexane. Glpc analysis of the reaction mixture after isolation from the excess bromine and hydrogen bromide showed only the presence of 1-, 2- and 3-bromo-1-chloroperdeuteriobutane and the unbrominated starting material (Table 14). The products were identified by comparison of their glpc retention times with those of authentic protiated materials. No 1,2-dibromoperdeuteriobutane was detected in any of the reactions. The material balance on recovered organic material was between 91 and 98%.

A synthetic mixture, whose composition corresponded to the mixture of products and reactants obtained in reaction 2 (Table 14), with the addition of 4-bromo-1-chlorobutane (7.95×10^{-6} M) and a 1:2.7 mixture of 1,2-dibromo-3-chlorobutane and 2,3-dibromo-1-chlorobutane (3.42×10^{-6} M), was introduced, in the absence of light,

Table 14

Photobromination of Perdeuterio-1-chlorobutane with Excess Bromine and Hydrogen Bromide in the Vapour Phase (22ℓ)

	(Concentration mol/ℓ x 10^5)		
Reactants[a]	1	2	3
$[RD(H)]^{\circ}$	21.34	23.68	22.34
$[Br_2]^{\circ}$	40.23	42.82	40.82
$[HBr]^{\circ}$	306.1	359.9	325.7
$[R^{\alpha}H]^{\circ}$	0.89	0.97	0.91
$[R^{\beta}H]^{\circ}$	0.34	0.37	0.34
$[R^{\gamma}H]^{\circ}$	1.04	1.14	1.09
$[R^{\delta}H]^{\circ}$	1.58	1.74	1.63
Products[a,b]			
$[RD(H)]$	19.72	20.54	18.71
$[R^{\alpha}H]$	0.91	1.02	0.97
$[R^{\beta}H]$	0.41	0.60	0.63

continued.....

Table 14 (cont'd.)

Products[a,b]	(Concentration mol/ℓ x 10^5) 1	2	3	
$[R^{\gamma}H]$	1.31	1.93	1.68	
$[R^{\delta}H]$	1.60	1.85	1.69	
$[R^{\alpha}Br]$	0.17	0.46	0.41	
$[R^{\beta}Br]$	0.16	0.50	0.40	
$[R^{\gamma}Br]$	0.27	0.74	0.66	
$[R^{\delta}Br]$[c]	0.00	0.00	0.00	
Relative Rate Constants				Average
k_{Br_2}/k_{HBr}[d]	12.0	12.1	11.7	11.9 ± 0.2
k_2/k_{-1}	64.7	77.3	54.5	65.5 ± 7.9
k_4/k_{-3}	17.4	18.3	11.0	15.6 ± 3.0
k_6/k_{-5}	7.6	7.9	8.9	8.1 ± 0.5
k_8/k_{-7}	<0.61	<0.12	<0.21	<0.31 ± 0.20

continued.....

Table 14 (cont'd.)

Relative Rate Constants	1	2	3	Average
k_1/k_5	0.33	0.33	0.37	0.34 ± 0.02
k_3/k_5	0.43	0.48	0.55	0.49 ± 0.04
k_7/k_5[e]	0.03	0.05	0.03	0.04 ± 0.01
Temp (°C)	22.7	22.8	23.1	

[a] [RD(H)] refers to the concentration of perdeuterio-1-chlorobutane, and $[R^iH]$ is the average concentration of the residual protium at position i.

[b] The values for $[R^iH]$ at the end of the reaction were calculated as:

$[R^iH]° + 1/2([RD(H)]° + [RD(H)]) \times$ (fractional incorporation of H at position i).

[c] Not detected by glpc.

[d] Relative rate of transfer of perdeuteriochlorobutyl radicals with bromine and hydrogen bromide.

[e] Per H atom.

into the reaction vessel and subjected to the same isolation and analysis procedure. The yield of recovered organic material was 94%; the yield of brominated chlorides was greater than 97% for all four monobrominated materials, and for the trihalide was greater than 99%. The ratio of all products was the same within the limits of the glpc analysis (±2%).

The unbrominated substrate was collected by preparative glpc and the amount of incorporated protium at each position was determined from a comparison of the H^1 100 MHz spectrum of the residual protium in the (Merck, Sharp and Dohme 98.4 atom % D) starting material and the spectrum of the recovered perdeuterio-1-chlorobutane (see Fig. 3 and 4). The total amount of protium was determined by mass spectrometry for reactions 2 and 3 (Table 14), the amount at each position being obtained from the ratio of the nmr signals of the different hydrogens. The nmr method, using 1,1-diphenylethene as standard, was used to determine the amount of protium in each position for the starting material and the recovered unbrominated substrate for reaction 1 (see experimental section).

The relative rates of transfer with bromine and with hydrogen bromide for perdeuterio-1-chlorobutyl radicals was calculated as 11.9 ± 0.2; therefore, in "normal"

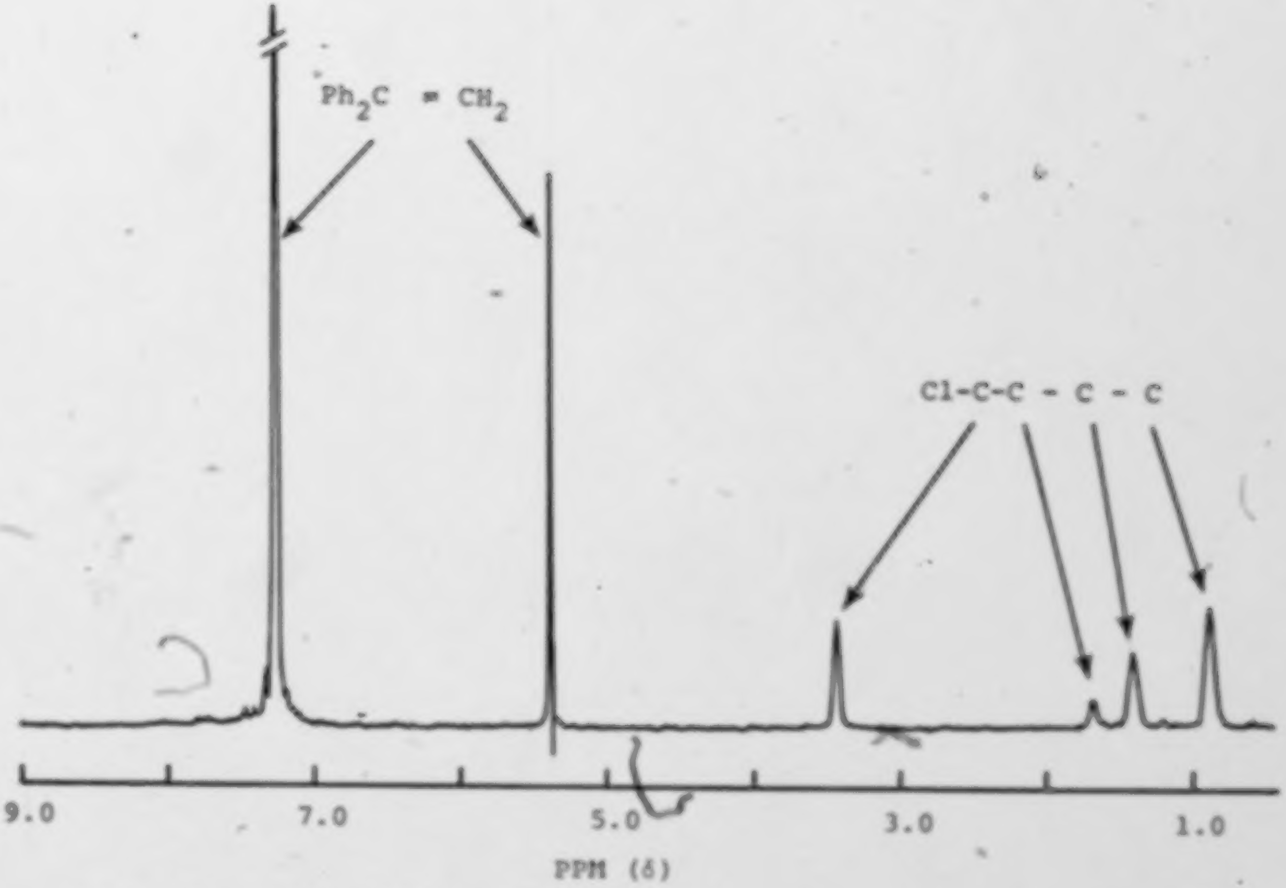


Fig. 3. NMR Spectrum of a Mixture of Perdeuterio-1-Chlorobutane (before reaction) and 1,1-Diphenylethene (Freon 113, TMS internal reference)

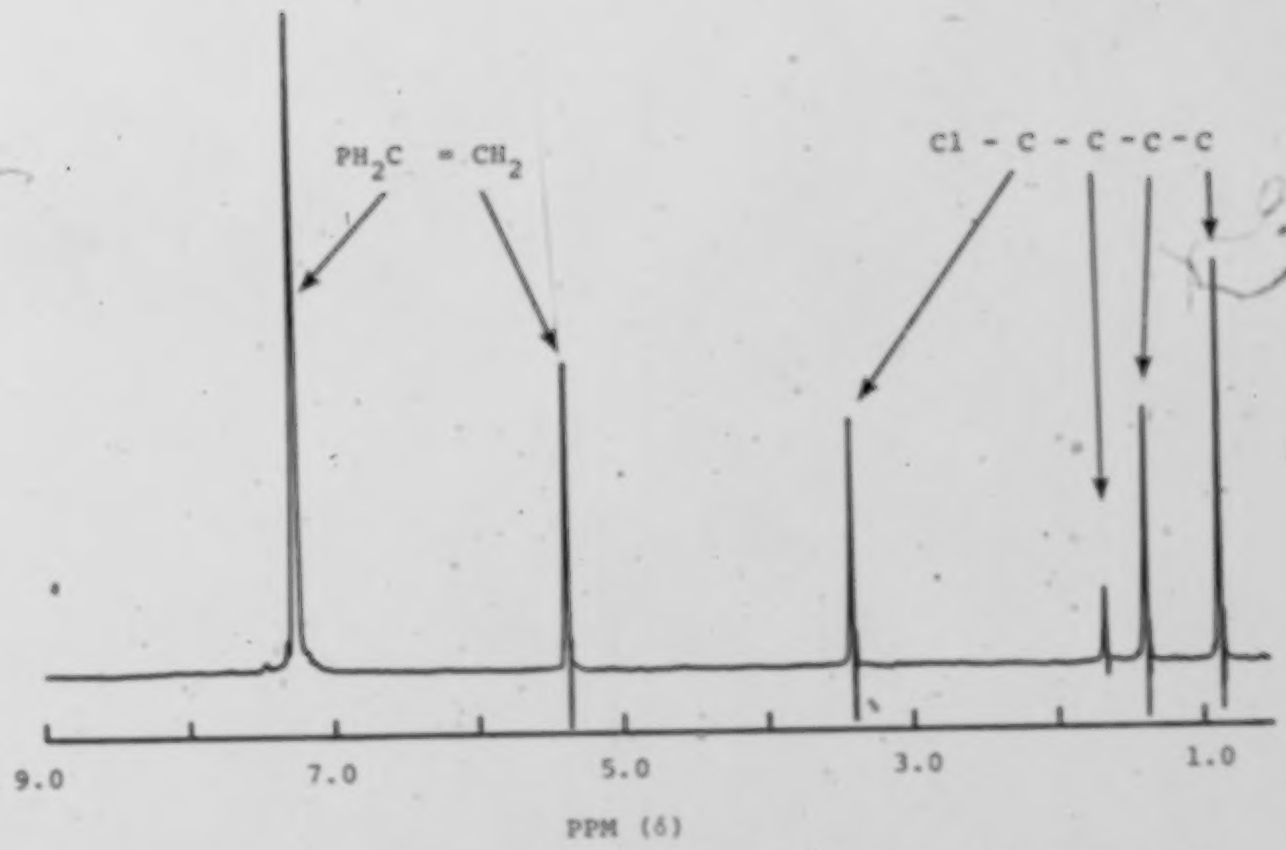


Fig. 4. Deuterium Decoupled Spectrum of a Mixture of Perdeuterio-1-Chlorobutane (before reaction) and 1,1-Diphenylethene (Freon 113, TMS internal reference)

brominations at 50% conversion of bromine, where the concentrations of bromine and hydrogen bromide are equal, only 7.9% of the radicals transfer with hydrogen bromide. The smaller percentage that reverse compared to that of perdeuteriocyclohexyl radicals (26%) is due presumably to the deactivation of the molecule by the chlorine substituent in the transfer with hydrogen bromide, and, by the principle of microscopic reversiblilty, in the abstraction of deuterium from perdeuterio-1-chlorobutane by bromine atoms.

The relative rates of transfer of the isomeric perdeuterio-1-chlorobutyl radicals with bromine and with hydrogen bromide were determined using equation 23 (Table 14). The ratio k_8/k_{-7} (Scheme 1) could not be calculated directly for the δ-position, since 4-bromo-1-chloroperdeuteriobutane was not detected in the three reactions. Since controls showed that a concentration of 1.6×10^{-8} M of 4-bromo-1-chlorobutane would have been detected by glpc under the analytical conditions used, k_8/k_{-7} was calculated assuming that the concentration of this isomer was less than 10^{-8} M (Table 14).

The relative rates of transfer of the perdeuterio-1-chlorobutyl radicals with bromine and with hydrogen bromide fall off rapidly with the distance from the substituent, from 66 for the α-position to less than 0.3 for the δ-position. This change in relative rates may be rationalized on the basis of a polar deactivation to transfer with hydrogen bromide, the deactivation falling off as the distance from the electronegative substituent increases. Transfer with molecular bromine, however, is little influenced by polar effects.

The rates of deuterium abstraction relative to the rate of abstraction of the γ-deuterium, calculated using equation 29 (Table 14), were also found to follow the order predicted for the reaction of a selective radical whose reactivity is strongly influenced by the polar effect of the substituent, i.e. α-H, 0.34, < β-H, 0.49, < γ-H, 1.00, > the primary δ-H, 0.04. The reactivity of the α-hydrogens is higher than one would expect on the basis of polar effects, since this position suffers the largest inductive deactivation, as shown by the very large k_2/k_{-1} ratio of 66. The higher reactivity must be due to the lower C-D bond strength (due to electron withdrawal by the chlorine substituent) and to the stablization of the radical formed by resonance with the chlorine atom (structure $\underset{\sim}{2b}$, page 4).

The relative rates of abstraction from perdeuterio-1-chlorobutane and from 1-chlorobutane in the gas phase were also determined by stopping the bromination with no initially added hydrogen bromide at very low conversion. Under these conditions, the concentration of hydrogen or deuterium bromide was very small compared to that of bromine, and therefore reversal was not expected to be important. The ratio of brominated chlorides should then reflect the rates of abstraction of the different hydrogens (or deuteriums) in the molecule. The results are given in Table 15; they are in very good agreement with each other and with those calculated from the data of Table 14. The coincidence between the values for 1-chlorobutane and its perdeuterated analog shows that deuterium kinetic isotope effects are not important in the relative rates of abstraction, and substantiates the assumption in equation 30.

II.3.2 Bromination of 1-Chlorobutane under "Normal" Conditions in the Vapour Phase

A second test of the kinetic data obtained from perdeuterio-1-chlorobutane and for the proposed mechanism (Scheme 1) was carried out. The bromination of a 9.8:1 molar mixture of 1-chlorobutane and molecular bromine ("normal" bromination) was run in the vapour phase and stopped at different stages of conversion. This particular ratio of reactants was chosen since preliminary experiments showed that at complete conversion of the bromine, no dibromochlorobutanes were formed. The products were isolated and analyzed by glpc (Table 16). From the results,

Table 15

Photobromination of 1-Chlorobutane and Perdeuterio-1-Chlorobutane in the Vapour Phase (5 ℓ) Under Irreversible Bromination Conditions

$[C_4H_9Cl]^a$	$[Br_2]^a$	Temp. °C	% Reaction[a]	$\frac{[Br_2]}{[HBr]}^b$	$R^{\alpha}Br^c$	$R^{\beta}Br^c$	$R^{\gamma}Br^c$
0.52	6.12	23	3.2	400	0.36	0.48	1.00
8.08	0.83	24	4.5	21	0.36	0.47	1.00
8.08	0.83	24	9.2	10	0.36	0.42	1.00
1.42[d]	1.32	22	7.0	13	0.40	0.44	1.00

[a] Concentration M, x 10^4. % Reaction based on bromine, except for the first reaction.

[b] Final ratio of bromine/hydrogen bromide.

[c] Ratio of 1-bromo-($R^{\alpha}Br$) and 2-bromo-1-chlorobutane ($R^{\beta}Br$) to 3-bromo-1-chlorobutane ($R^{\gamma}Br$). The material balance on 1-chlorobutane was always greater than 97%. Values quoted are ± 0.02.

[d] Perdeuterio-1-chlorobutane was used for this reaction.

Table 16

Photobromination of 1-Chlorobutane (8.080×10^{-4} M) with Molecular Bromine (8.262×10^{-5} M) in the Vapour Phase (5ℓ).

		Products[a]							
% Rn	Temp.	$R^{\alpha}Br$	$R^{\beta}Br$	$R^{\gamma}Br$	x^{b}	$f^{\alpha/\gamma}_{obs}$	$f^{\alpha/\gamma}_{calc}$	$f^{\beta/\gamma}_{obs}$	$f^{\beta/\gamma}_{calc}$
4.5	23.9°	0.078	0.098	0.218	21.13	0.363	0.352	0.466	0.481
9.2	24.2°	0.152	0.190	0.420	9.910	0.358	0.354	0.424	0.483
20.0	24.8°	0.324	0.402	0.880	3.998	0.397	0.359	0.489	0.487
27.4	24.6°	0.480	0.588	1.250	2.649	0.402	0.364	0.504	0.491
43.6	25.0°	0.742	0.926	2.592	1.296	0.406	0.379	0.517	0.500
60.9	24.8°	1.232	1.032	2.752	0.6415	0.441	0.407	0.512	0.519
71.0	23.8°	1.422	1.248	3.162	0.4086	0.491	0.439	0.538	0.539
82.7	23.8°	1.652	1.482	3.582	0.2092	0.626	0.516	0.584	0.583
90.3	22.8°	1.818	1.628	3.824	0.1069	0.748	0.672	0.622	0.648

[a] Concentration in mol/ℓ, x 10^{5}. % Reaction based on bromine.

[b] $[Br_2]/[HBr]$ ratio.

plots of the concentration of 1-bromo-1-chlorobutane ($R^{\alpha}Br$), 2-bromo-1-chlorobutane ($R^{\beta}Br$) and 3-bromo-1-chlorobutane ($R^{\gamma}Br$) against $[Br_2]/[HBr]$, (x), were constructed. The experimental values obtained from the "normal" brominations were fitted manually and by a least squares method to an exponential function (equation 56), and the

$$R^{i}Br = ae^{-bx} + ce^{-2bx} + de^{-3bx} + fe^{-4bx} \qquad (56)$$

ratios of the slopes obtained by graphical differentiation from these synthesized curves gave the observed values of the functions $(d[R^{\alpha}Br]/dx)/(d[R^{\gamma}Br]/dx)$ (Figure 5) and $(d[R^{\beta}Br]/dx)/(d[R^{\gamma}Br]/dx)$ (Figure 6) for any value of x.

The values of these functions at any value of x were also calculated using the relative rate data obtained for perdeuterio-1-chlorobutane (Table 14), from two equations of the type of equation 33. A comparison of the calculated and the experimentally obtained values of these functions is given in figures 5 and 6.

The error limits shown in these figures for the calculated values of $f^{\alpha/\gamma}$ and $f^{\beta/\gamma}$ (equation 33) were obtained using the maximum and minimum values reported for the relative rates of transfer and abstraction (Table 14). When the error limits were included for the experimental data (± 2%, glpc error) used to determine the observed

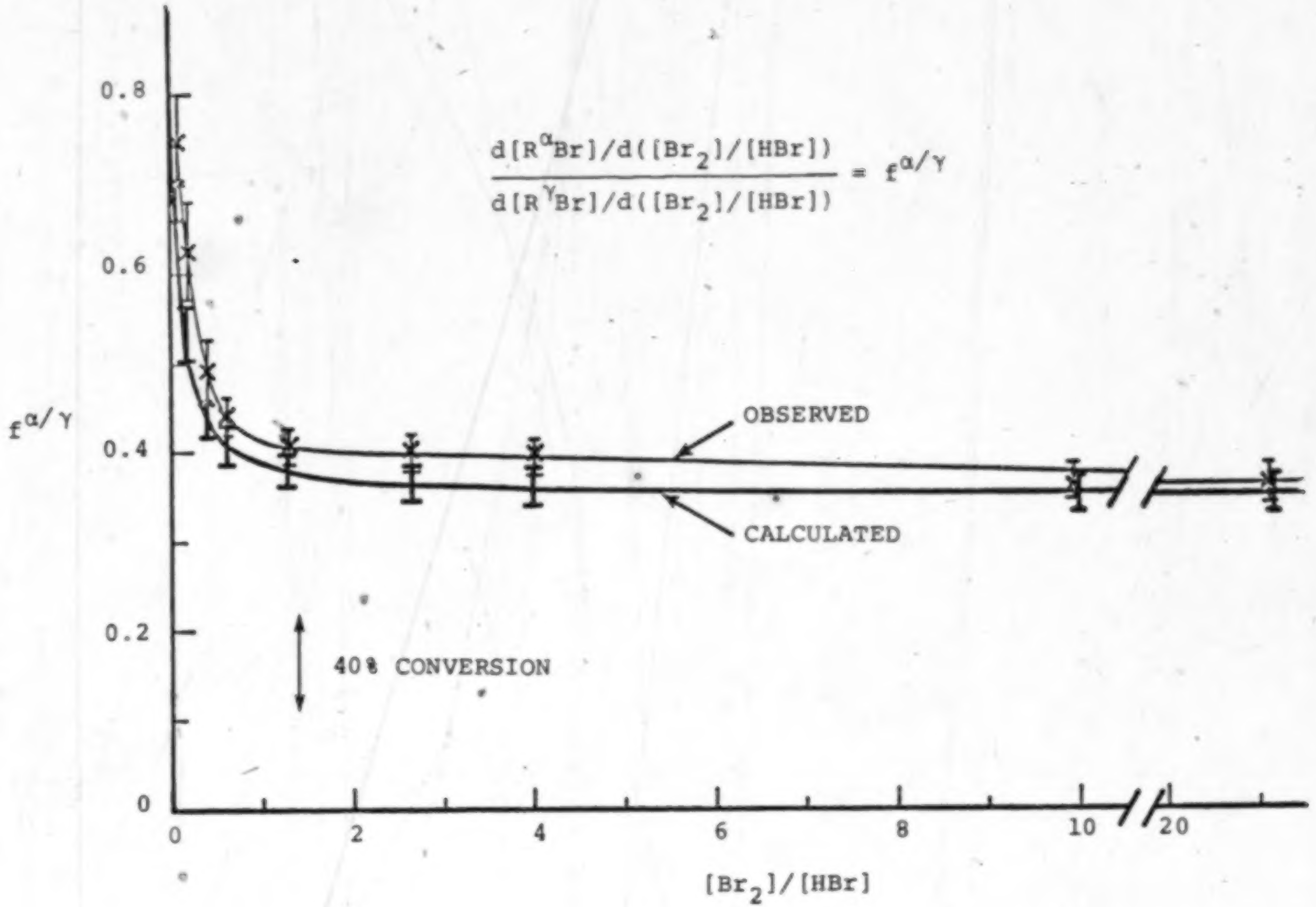


Fig. 5. Plot of the Observed and Calculated $f^{\alpha/\gamma}$ vs $[Br_2]/[HBr]$ for the Photobromination of 1-Chlorobutane in the Vapour Phase

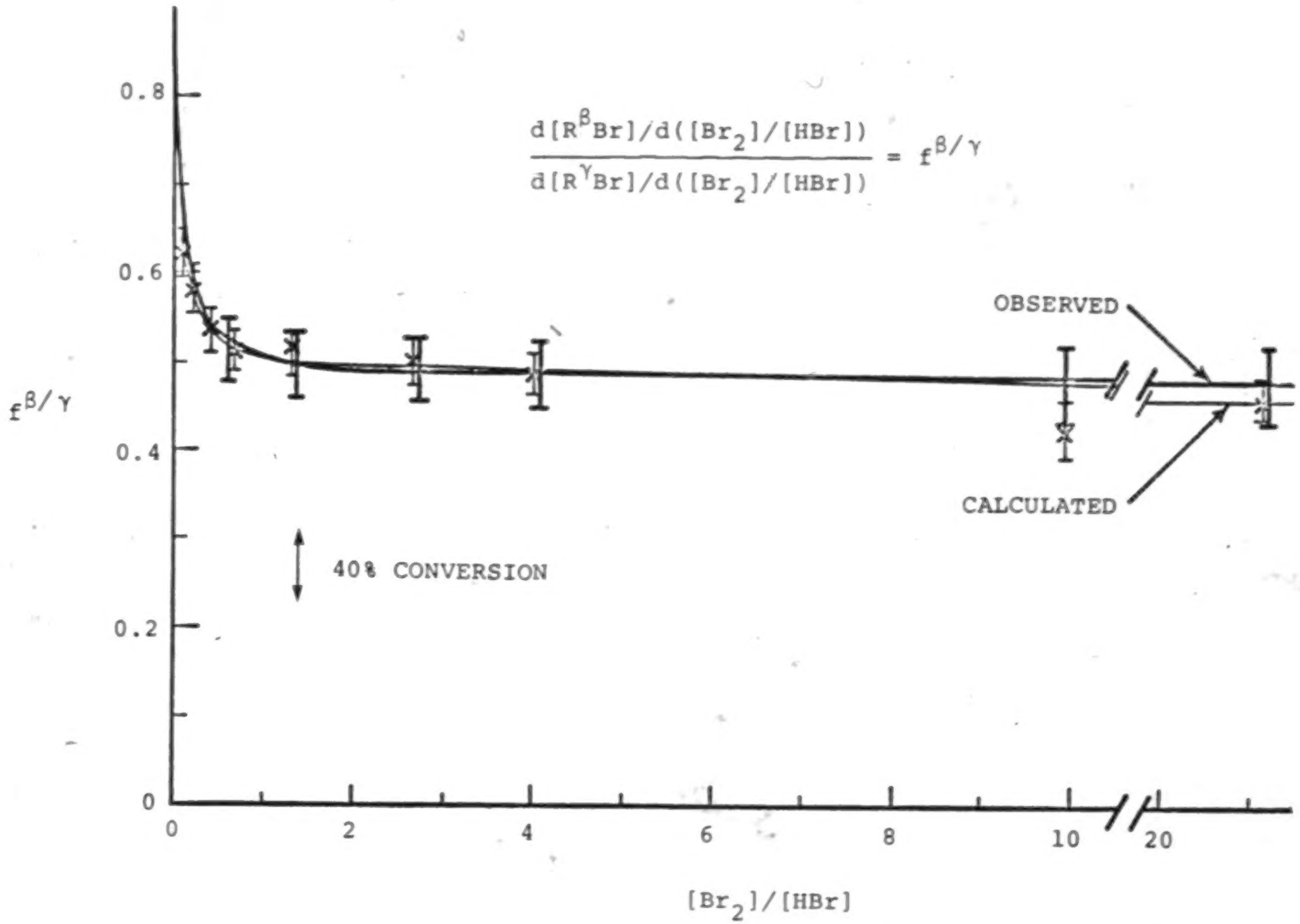


Fig. 6. Plot of the Observed and Calculated $f^{\beta/\gamma}$ vs $[Br_2]/[HBr]$ for the Photobromination of 1-Chlorobutane in the Vapour Phase.

values of $f^{\alpha/\gamma}$ and $f^{\beta/\gamma}$, the observed and calculated functions were found to be coincident within the experimental limits.

The coincidence of the calculated values of $f^{\alpha/\gamma}$ and $f^{\beta/\gamma}$ with those of the experimentally determined values demonstrates that the relative rate data obtained for perdeuterio-1-chlorobutane describe adequately the kinetic behaviour of the "normal" bromination of 1-chlorobutane in the vapour phase, and shows that the assumption proposed in equation 30 must hold.

Figures 5 and 6 demonstrate the different relative rates of transfer with bromine and with hydrogen bromide of the isomeric chlorobutyl radicals. After 40% conversion of the bromine, or when $x \leqslant 1.5$, the rate of formation of 1-bromo-1-chlorobutane and 2-bromo-1-chlorobutane increases rapidly relative to the rate of formation of 3-bromo-1-chlorobutane. This is expected, since due to polar effects, the γ-chlorobutyl radicals are expected to reverse with hydrogen bromine at the fastest rate. Consequently, as the concentration of the hydrogen bromide builds up, reversal with it starts affecting the distribution of products observed.

II.3.3 Comparison of Liquid and Vapour Phase Results

The photobromination of perdeuterio-1-chlorobutane with excess bromine and with added hydrogen bromide in Freon 113 solution at 23° was studied in these laboratories.[110] On the basis of the results obtained from perdeuteriocyclohexane, the liquid phase reaction should be complicated not only by reversal of the radicals with hydrogen bromide, but also by cage filtering and by transfer of the radicals with hydrogen tribromide. If these effects were not important in the liquid phase photobromination of perdeuterio-1-chlorobutane, the mechanism in Scheme 1 would apply to the reaction, and the relative rates of transfer of the radicals with bromine and with hydrogen bromide, and the relative rates of abstraction of deuterium could be calculated from equations 23 and 29 respectively. The results obtained assuming this mechanism are given in Table 17, where they are compared with the vapour phase results.

If solvent effects on these relative rates are negligible, the liquid and vapour phase results should be the same. This is evidently not the case. The relative rates of transfer with bromine and with hydrogen bromide were lower in solution than in the vapour phase (as had been found with perdeuteriocyclohexane), while the relative

Table 17

Photobromination of Perdeuterio-1-chlorobutane with Excess Bromine and Excess Hydrogen Bromide in Freon 113[a]

	Concentration M, x 10^3 1	2		
Reactants[b]				
$[RD(H)]°$	13.3	20.2		
$[Br_2]°$	50.4	39.1		
$[HBr]°$	44.6	41.8		
Relative Rates[c]			Average	Vapour Phase[d]
$(k_2/k_{-1})^{obs}$	8.3	9.3	8.8 ± 0.5	65.5 ± 7.9
$(k_4/k_{-3})^{obs}$	6.1	6.7	6.4 ± 0.3	15.6 ± 3.0
$(k_6/k_{-5})^{obs}$	1.9	2.0	2.0 ± 0.1	8.1 ± 0.5
$(k_{Br_2}/k_{HBr}{}^{e})^{obs}$	2.8	2.7	2.8 ± 0.1	11.9 ± 0.2
$(k_1/k_5)^{obs}$	0.47	0.46	0.47 ± 0.01	0.34 ± 0.02
$(k_3/k_5)^{obs}$	0.54	0.52	0.53 ± 0.01	0.49 ± 0.04
$(k_7/k_5{}^{f})^{obs}$	0.05	0.04	0.04 ± 0.01	0.04 ± 0.01

continued.....

Table 17 (cont'd.)

[a] Taken from ref. 110; reactions were run at 23.0 ± 0.1°.

[b] $[RD(H)]^{\circ}$ refers to the initial concentration of perdeuterio-1-chlorobutane.

[c] Calculated assuming the mechanism in Scheme 1 (X=Cl) using equations 23 and 29.

[d] Taken from Table 14.

[e] Relative rate of transfer of perdeuterio-1-chlorobutyl radicals with bromine and with hydrogen bromide.

[f] Per hydrogen atom.

rates of abstraction were higher in solution than in the vapour phase. These results indicated that transfer with hydrogen tribromide and cage effects were not unimportant for the bromination of an electronegatively substituted alkane.

A detailed mechanistic scheme for the photobromination of perdeuterio-1-chlorobutane is given in Scheme 4. The relative rates of appearance of any two brominated products, e.g. $R^{\alpha}Br$ and $R^{\gamma}Br$, can be expressed as equation 57 (see Appendix 1). This equation was derived

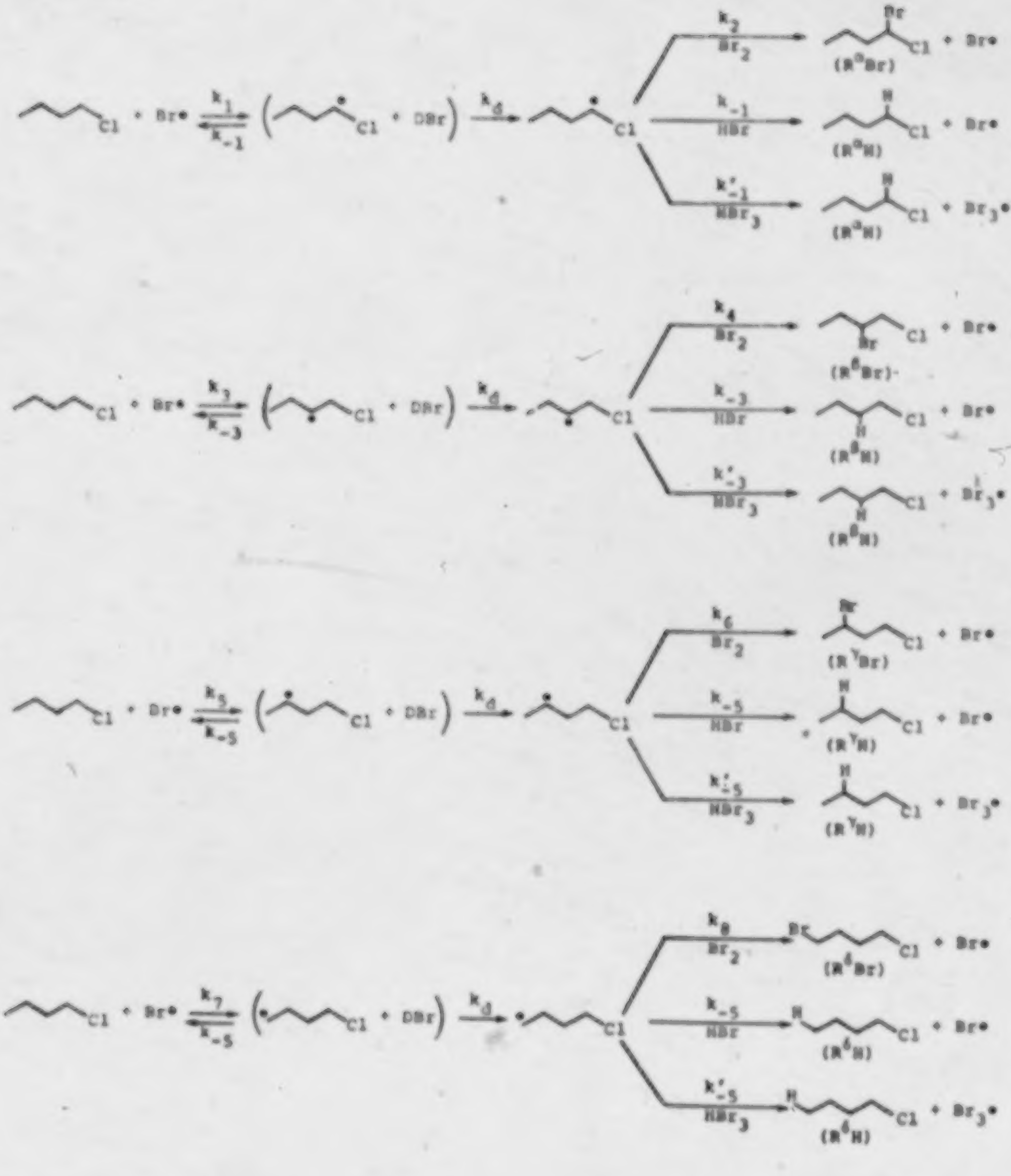
$$\frac{d[R^{\alpha}Br]/dt}{d[R^{\gamma}Br]/dt} =$$

$$\frac{k_1 k_2 (k^D_{-5}[DBr]^C + k_d)(k_{-5}[HBr] + k'_{-5}[HBr_3] + k_6[Br_2])}{k_5 k_6 (k^D_{-1}[DBr]^C + k_d)(k_{-1}[HBr] + k'_{-1}[HBr_3] + k_2[Br_2])} \qquad (57)$$

assuming steady state concentrations of both "free" and caged radicals and assuming that the rate of diffusion, k_d, was the same for the isomeric perdeuterio-1-chlorobutyl radicals. Equation 57 may be integrated under conditions where the concentrations of bromine and hydrogen bromide do not change significantly.

The relative rates of transfer of the "free" radicals may be evaluated by a study of the relative rates

Scheme 4


Cl
Br•
k1
k-1
DBr
kd
k2
Br2
k'-1
HBr
HBr3
(R^αBr)
(R^αH)
Br3•
k3
k-3
k4
k'-3
(R^βBr)
(R^βH)
k5
k-5
k6
k'-5
(R^γBr)
(R^γH)
k7
k8
(R^δBr)
(R^δH)

of product formation (R^iH and R^iBr) for each position of the starting material. The expression for the α-position is the same as that for perdeuteriocyclohexyl radicals (equation 36); those for the β- and γ-radicals are given by equations 58 and 59. These expressions may be integrated

$$\frac{d[R^{\beta}Br]/dt}{d[R^{\beta}H]/dt} = \frac{k_4([Br_2]^\circ - [HBr_3])}{k_{-3}([HBr]^\circ - [HBr_3]) + k'_{-3}[HBr_3]} \qquad (58)$$

$$\frac{d[R^{\gamma}Br]/dt}{d[R^{\gamma}H]/dt} = \frac{k_6([Br_2]^\circ - [HBr_3])}{k_{-5}([HBr]^\circ - [HBr_3]) + k'_{-5}[HBr_3]} \qquad (59)$$

when the concentrations of bromine, hydrogen bromide and hydrogen tribromide do not change significantly.

Using the value of the equilibrium constant for the formation of hydrogen tribromide at 23° obtained by nmr (section II.2.4), the value of $[HBr_3]$ could be determined, and thence, by substituting into equation 37 and the integrated forms of equations 58 and 59 the vapour phase values of the relative rates of transfer with bromine and with hydrogen bromide, the ratio of transfer of the different perdeuterio-1-chlorobutyl radicals with hydrogen tribromide and with hydrogen bromide could be calculated. The computed values for these ratios of rate constants were $k'_{-1}/k_{-1} = 56.5 \pm 1.8$ (α-radicals), $k'_{-3}/k_{-3} = 12.5 \pm 0.5$ (β-radicals), $k'_{-5}/k_{-5} = 27.2 \pm 1.8$ (γ-radicals). The value of this ratio for the γ-radicals is the same as that for perdeuteriocyclohexyl radicals, within experimental error ($k'_{-i}/k_{-i} = 22 \pm 7$, section II.2.5). This was not surprising since of all the isomeric perdeuteriochlorobutyl radicals, the γ-radicals should be most similar to the perdeuteriocyclohexyl radicals.

By a combination of the integrated forms of, e.g. equations 36 and 57, expression 60 may be obtained (see Appendix 1) that will allow an experimental evaluation of

$$C^{\alpha}_{\gamma} = \frac{(k^{D}_{-1}[DBr]^{c} + k_{d})}{(k^{D}_{-5}[DBr]^{c} + k_{d})} = \frac{k_{1}(\Delta[R^{\gamma}H] + [R^{\gamma}Br])}{k_{5}(\Delta[R^{\alpha}H] + [R^{\alpha}H])} \qquad (60)$$

cage filtering, C^{i}_{j}. The cage effect may be determined from the results of the bromination of perdeuterio-1-chlorobutane if one invokes the assumption proposed by Mayo[19] that there will be negligible solvent effects on the relative rates of abstraction and transfer of competing free radical reactions of the same kinetic order in inert solvents. By combining the vapour and liquid phase results, $C^{\alpha}_{\gamma} = 0.72 \pm 0.05$, $C^{\beta}_{\gamma} = 0.92 \pm 0.07$, $C^{\gamma}_{\gamma} = 1.00$, $C^{\delta}_{\gamma} = 1.0 \pm 0.5$.

The cage effects should follow the same trend as that observed for the relative rates of transfer with bromine and with hydrogen bromide. As the radical center involved was further removed from the electron withdrawing chlorine substituent, the polar deactivation deceased. The cage effect is a competition with diffusion between two radicals for deuterium bromide, and since from the above reasoning $k^D_{-1} < k^D_{-3} < k^D_{-5} < k^D_{-7}$, the cage effect, C^i_j, should increase from C^α_γ to C^δ_γ. This trend is actually followed from C^α_γ to C^γ_γ; however C^δ_γ was the same as C^γ_γ (1.0 ± 0.5 vs 1.0). The calculated value for the ratio of the transfer rates of the δ-radicals with bromine and with hydrogen bromide (< 0.31) was the smallest one of the four isomeric radicals (see Table 14). This indicates that if the rate of transfer of these radicals with molecular bromine is not much influenced by polar effects, the δ-radicals should reverse with hydrogen bromide at the fastest rate. It is probable that C^δ_γ is larger than C^γ_γ, but the data is not accurate enough to reflect this. It must be noted that perdeuterio-4-bromo-1-chlorobutane was not detected in these brominations either in Freon 113 or in the vapour phase; the rate data for the δ-position was therefore calculated from the amount of protium incorporated at this position only.

The liquid phase photobromination of 1-chlorobutane was also studied, using conditions where, on the basis of the results from the relative rates of bromination of cyclohexane and perdeuteriocyclohexane, there was no external and internal reversal (~11 M bromine) and no external reversal (~0.6 M bromine, and ensuring $[Br_2]/[HBr] >> 1$), Table 18. The reactions were run to low percent conversion of 1-chlorobutane; the unreacted bromine was destroyed with aqueous sodium bisulphite, and the products analyzed by glpc. Only 1-bromo-, 2-bromo-, and 3-bromo-1-chlorobutane were detected, and a control reaction showed that these products were stable in the absence of light in 12 M bromine solution under the reaction conditions.

The relative rates of abstraction from 1-chlorobutane in liquid bromine were found to be in remarkable agreement with the relative rates of abstraction from perdeuterio-1-chlorobutane in the vapour phase and the relative rates of abstraction from 1-chlorobutane in the vapour phase bromination run to low percentage reaction (see Table 19). This coincidence was not surprising: at the very high concentration of bromine used, the bromine should scavenge all the radicals formed, caged or "free". The agreement between these results gives further support to the assumption that any solvent effects on the relative rates of abstraction are not important.

When the bromine concentration was lower (0.6 M), where cage scavenging should not be important, and where

Table 18

Photobromination of 1-Chlorobutane in the Liquid Phase[a]

Reaction #	Concentration, M $[C_4H_9Cl]°$	$[Br_2]°$	Temp. °C	% Conversion[b]	$R^{\alpha}Br$	$R^{\beta}Br$	$R^{\gamma}Br$
1	0.219	0.556	21.0	2	0.55	0.55	1.00
2	0.219	0.556	21.0	3	0.49	0.54	1.00
3	0.219	0.556	21.0	4	0.54	0.55	1.00
4	0.217	0.567	23.0	1	0.51	0.51	1.00
5	0.217	0.567	23.0	1	0.53	0.56	1.00
6	0.217	0.567	23.0	3	0.49	0.53	1.00
7	0.217	0.567	23.0	4	0.50	0.53	1.00
8	0.217	0.567	23.0	10	0.52	0.53	1.00
9	2.60	10.3	21.0	2	0.31	0.47	1.00
10	2.60	10.3	21.0	3	0.35	0.47	1.00
11	0.199	11.6	21.0	1	0.31	0.48	1.00
12	0.199	11.6	21.0	1	0.33	0.47	1.00

continued......

Table 18 (cont'd.)

[a] Reactions 1-8 were run in Freon 113 solvent; reactions 9-12 were run in liquid bromine solvent.

[b] Based on 1-chlorobutane.

Table 19

Comparison of the Vapour and Liquid Phase Results from the Photobrominations of 1-Chlorobutane and Perdeuterio-1-chlorobutane

Conditions	$R^{\alpha}Br$	$R^{\beta}Br$	$R^{\gamma}Br$	C^{α}_{γ}	C^{β}_{γ}
Vapour phase, 1-chlorobutane, 24°, 4.5% reaction[a]	0.36±0.02	0.45±0.02	1.0		
Calculated from the vapour phase rates of perdeuterio-1-chlorobutane[b]	0.34±0.02	0.49±0.04	1.0		
Liquid bromine, 21°, 1-3% reaction of 1-chlorobutane[c]	0.33±0.02	0.47±0.01	1.0		
Freon 113, 23°, 1-10% reaction of 1-chlorobutane[c]	0.51±0.01	0.53±0.01	1.0		

continued.....

Table 19 (cont'd.)

Conditions	$R^{\alpha}Br$	$R^{\beta}Br$	$R^{\gamma}Br$	C^{α}_{γ}	C^{β}_{γ}
Cage effect for 1-chlorobutane, calculated from equation 61				0.65±0.05	0.89±0.03
Calculated for perdeuterio-1-chlorobutane from equation 60				0.72±0.05	0.92±0.07

[a] Taken from Table 16.

[b] Taken from Table 14.

[c] Taken from Table 18.

external reversal was negligible ($[Br_2]/[HBr] > 20$), the isomer distribution at low conversion of 1-chlorobutane was different from that obtained in liquid bromine. This was expected, since under these conditions, cage filtering distorts the relative concentrations of "free" radicals, relative to the concentrations formed on abstraction.

Under the conditions of the latter reactions, i.e. when there was internal reversal but no external reversal, the expression for the cage effect (the counterpart of equation 60 for normal 1-chlorobutane) becomes equation 61. Using the value for k_i/k_j obtained from the

$$C_j^i = \frac{(k_{-i}^H[HBr]^c + k_d)}{(k_{-j}^H[HBr]^c + k_d)} = \frac{k_i[R^jBr]}{k_j[R^iBr]} \qquad (61)$$

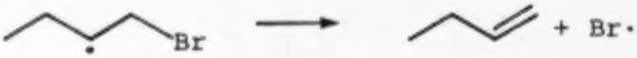
brominations at high bromine concentrations, and the value for $[R^iBr]/[R^jBr]$ from the reactions with 0.6 M bromine, the cage effect was evaluated from equation 61 (Table 19). The agreement between the cage effect calculated for perdeuterio-1-chlorobutane (by a combination of vapour and liquid phase results) and for the natural protiated substrate (using liquid phase results only) supports the assumptions made and gives confidence in the reliability of the relative rates obtained in these bromination reactions.

II.4 1-Bromobutane

The bromination of 1-bromobutane has had an eventful history and has been the subject of a large number of investigations. The reaction gives unique product distributions both in the liquid and in the vapour phase, though most studies have been concerned with the solution phase reaction, and have tended to neglect the results obtained in the gas phase.

The reaction appears to have been first studied in 1956 by Kharasch in his systematic studies of the vapour phase photobromination of simple bromo- and chloro-alkanes.[109] Four products were detected when the reaction was run at 100° using a 2.8:1 mol ratio of 1-bromobutane to bromine: 1,2-dibromobutane (30%), 1,3-dibromobutane (13%), an unidentified tribromide (30%) and 1,2,3,4-tetrabromobutane (10%). The large yield of polybromides is surprising, as well as the ratio of 1,2- to 1,3-dibromobutane (2.3:1), since polar effects should direct attack preferentially to the 3-position (cf. Table 1). These anomalies went mainly unnoticed in the literature.

In 1960, Tedder and Fredricks attempted to study the reaction in the vapour phase using a flow system at 78° and 146°; the reaction was reported to be strongly inhibited by some product of the reaction. A large portion of the bromine failed to react and the sides of the vessel became coated with a brown film. This was attributed to the formation of olefinic material by loss of bromine from the β-bromobutyl radical (reaction 62).[13]



(62)

A few years later, Thaler studied the liquid phase reactions.[66] Thaler noted that solution phase brominations of bromoalkanes gave abnormally large amounts of vicinal dibromide; thus, the reaction of a 5:1 mol ratio of 1-bromobutane and bromine at 60° with no solvent gave 1,1-dibromobutane (0.9%), 1,2-dibromobutane (84.6%) and 1,3-dibromobutane (14.6%). This unexpected result (cf. Table 1) was found to be common with a large number of brominations of bromoalkanes, and Thaler proposed anchimeric assistance by the bromine substituent in the transition state for abstraction of the β-hydrogen, giving a bridged bromine intermediate, which is trapped by bromine to give the vicinal dibromide to explain the results. Since bromination reactions are usually endothermic and have a high activation energy, the reactions should be very sensitive to any process that lowers the activation energy; the stability given to the transition state for the abstraction of the β-hydrogen and to the intermediate by delocalization of the unpaired electron would increase the rate of attack at that position, thereby enhancing the formation of the vicinal dibromide relative to the other possible isomers.

The concept of anchimeric assistance in the bromination of bromoalkanes was generally accepted in the literature. Skell extended the evidence for this proposal: this has been amply discussed elsewhere,[79-81] and will not be reviewed here. However, recently the concept has been questioned.[44,52,53,75,78,82-85]

Tanner et al. studied the bromination of 1-bromobutane with molecular bromine and reported that the distribution of products was a function of the percentage reaction (Table 20).[78] At low conversion, the distribution of dibromides was similar to that found in the bromination and chlorination of other electronegatively substituted butanes (cf. Table 1); as the reaction progressed, the amount of 1,2-dibromobutane increased until at complete consumption of bromine, it made up 88% of all the products. It was suggested that this change in isomer distribution was due to equilibration of the initially formed radicals with hydrogen bromide and to elimination of bromine atoms from the β-bromobutyl radicals (see pages 31-32).

An attempt was made to minimize the effect of

Table 20

Product Distribution in the Bromination of 1-Bromobutane Under Different Conditions

Phase or Solvent	Brominating Agent, X	Molar Ratio, BuBr:X	Temp. °C	$R^{\alpha}Br$	$R^{\beta}Br$	$R^{\gamma}Br$	Ref.
Gas Phase	Br_2	2.8:1	100	-	2.2	1.0	109
1-Bromobutane	Br_2	5:1	60	0.09	5.78	1.0	66
1-Bromobutane[a]	Br_2	6:1	30	0.52	0.53	1.0	78
1-Bromobutane[b]	Br_2	6:1	30	tr	7.30	1.0	78
Acetronitrile[a]	NBS	4:1	30	0.19	0.29	1.0	78
Acetonitrile[b]	NBS	4:1	30	tr	5.51	1.0	78
Gas Phase[a]	Br_2	4.8:1	100	tr	0.29	1.0	82
Gas Phase[b]	Br_2	4.8:1	100	0.15	2.2	1.0	82
Gas Phase[c]	Br_2	4.8:1	100	0.33	7.7	1.0	82
1-Bromobutane[a]	Br_2	6:1	60	-	4.55	1.0	112
1-Bromobutane[a]	Br_2	6.8:1	25	0.1	7.6	1.0	111

continued.....

Table 20 (cont'd.)

Phase or Solvent	Brominating Agent, X	Molar Ratio, BuBr:X	Temp. °C	$R^{\alpha}Br$	$R^{\beta}Br$	$R^{\gamma}Br$	Ref.
Dichloromethane[d]	NBS-Br_2	10:1	30	-	7.55	1.0	113
Bromine	Br_2	0.01:1	60	tr	5.1	1.0	114

[a] Results at low conversion of brominating agent.

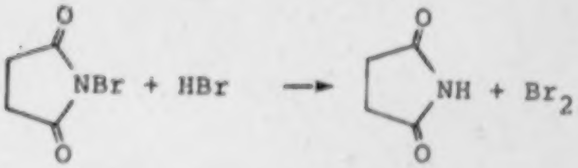
[b] Results at high conversion of brominating agent.

[c] Reaction was run with added hydrogen bromide.

[d] The NBS:Br_2 ratio was 1.0:0.0075.

hydrogen bromide on the product distribution by carrying out the bromination of 1-bromobutane with N-bromosuccinimide. By utilizing the previously established chain mechanism for bromination with NBS (reactions 63-65), it was anticipated that the hydrogen bromide concentration could be kept low enough to severely limit the reverse reaction.[78]

$$RH + Br\cdot \longrightarrow R\cdot + HBr \qquad (63)$$



(64)

$$R\cdot + Br_2 \longrightarrow RBr + Br\cdot \qquad (65)$$

This attempt was most successful when the reaction was carried out in homogeneous acetonitrile solution: at low conversion of the NBS, the product distribution was similar to that obtained with molecular bromine at low conversion (Table 20). However, the product distribution was found to change with percentage reaction in the bromination with NBS as well, and at complete reaction, 1,2-dibromobutane made up 85% of the products. This was attributed to reversal with hydrogen bromide when the NBS concentration was low. These results were strong evidence against the possibility of anchimeric assistance in the brominations of bromoalkanes.[78]

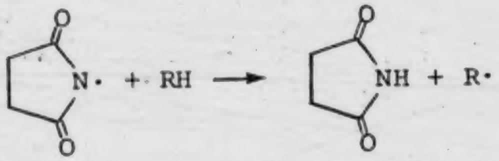
Independent support for these results came from a reinvestigation of the vapour phase bromination of 1-bromobutane with molecular bromine in a static system.[82] Tedder et al. found, in agreement with the above results, a change in the product distribution as the reaction progressed (Table 20). The ratio of 1,2-/1,3-dibromobutane changed from 0.28 after 10 minutes reaction time to 2.20 after 120 minutes. Addition of hydrogen bromide was found to drastically change the product distribution, so that, after 10 minutes reaction time, the ratio of 1,2- to 1,3-dibromobutane was 7.7.

The effect of hydrogen bromide on the bromination of electronegatively substituted alkanes (e.g., 1-bromobutane) has been rationalized in the following manner. During the initial stages of the reaction, the reversal reaction would be unimportant because of the low concentration of hydrogen bromide, and hence the transfer of the bromoalkyl radicals with molecular bromine would reflect the kinetically determined distribution of isomeric radicals. As the reaction proceeds, equilibration of the radicals with hydrogen bromide could occur. It was reasoned that if polar effects determined the kinetic distribution of radical abstraction, then, by the same token, the reverse reaction with hydrogen bromide should be subject to the same polar effects (microscopic reversibility). Therefore, the β-radicals are not only formed more slowly but likewise reverse more slowly and the 1,2-dibromide is formed since the non-polar bromine molecule is not subject to these polar effects. Elimination from the β-bromoalkyl radicals would further enhance the formation of the vicinal dibromides (pages 31-32).[78]

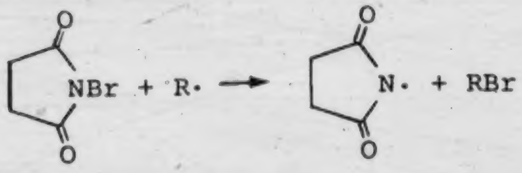
Recently, two communications have appeared questioning the previously reported result that in the bromination of 1-bromobutane with molecular bromine, at less than 20% conversion, the ratio of 1,2- to 1,3-dibromobutane was less than unity.[111, 112] Both groups noted a change in the product distribution with percentage reaction, although the effect was nowhere near as great as previously reported; in both communications, the ratio of 1,2- to 1,3-dibromobutane was greater than 1 at all stages of the reaction. Likewise, it was reported from this laboratory that the previous observation that this ratio was less than unity at low percentage reaction could not be repeated.[44]

The results obtained in the NBS bromination of 1-bromobutane in acetonitrile have been confirmed in this laboratory[103] and independently by Traynham et al.[111] Skell and Shea[112,113] however reported that the photobromination of 1-bromobutane with NBS in dichloromethane with a trace of bromine gave a product distribution that was different from that obtained in the reaction with NBS in acetonitrile, and similar to that obtained with molecular bromine as brominating agent.

The mechanism of NBS brominations of toluenes[16,39,41] and of alkenes[115] has been shown to proceed through a bromine atom chain. However, it was possible that in the endothermic brominations of alkanes and substituted alkanes, the NBS bromination was going through a succinimidyl radicals chain (reactions 66-67), as suggested recently by Traynham.[111,114] This possibility has been investigated in these laboratories.[44] The competitive photobromination of a number of alkanes and substituted alkanes with NBS in acetonitrile was



(66)



(67)

studied in detail. It was found that in these reactions, the substituted alkanes reacted at a slower rate than the parent alkane (see Table 3). When the brominations were run using other bromoamides (tetramethyl-N-bromosuccinimide, 1-bromo-3,5,5-trimethylhydantoin and 1,3-dibromo-5,5-dimethylhydantoin) in acetonitrile, the relative rates of bromination were similar to those obtained with NBS. Furthermore, when the photobrominations were run in liquid bromine (Table 3), the relative rates were very similar to those obtained using NBS in acetonitrile. The NBS rates in acetonitrile were also found not to change when these rates were run with some initially added molecular bromine ($R_1H:R_2H:NBS:Br_2$ = 1:1:8:0.4).[44] These results were taken as strong evidence that the alkylinic brominations of NBS in acetonitrile proceeded through a bromine atom chain.*

Anchimeric assistance is a rate acceleration which is due to the participation of a neighbouring atom or group with non-bonded electrons. A fundamental question in participation by the bromine substitutent in the abstraction of the β-hydrogens by bromine atoms is therefore the kinetic consequences. A detailed study of the gas phase photobromination of 1-bromobutane was therefore undertaken: Tedder's results had indicated that the bromination of 1-bromobutane in a static system in the gas phase gave the same product distributions as the disputed liquid phase reaction (cf. Table 20). It was therefore expected that an understanding of this vapour phase bromination would lead to an explanation of the conflicting liquid phase results.

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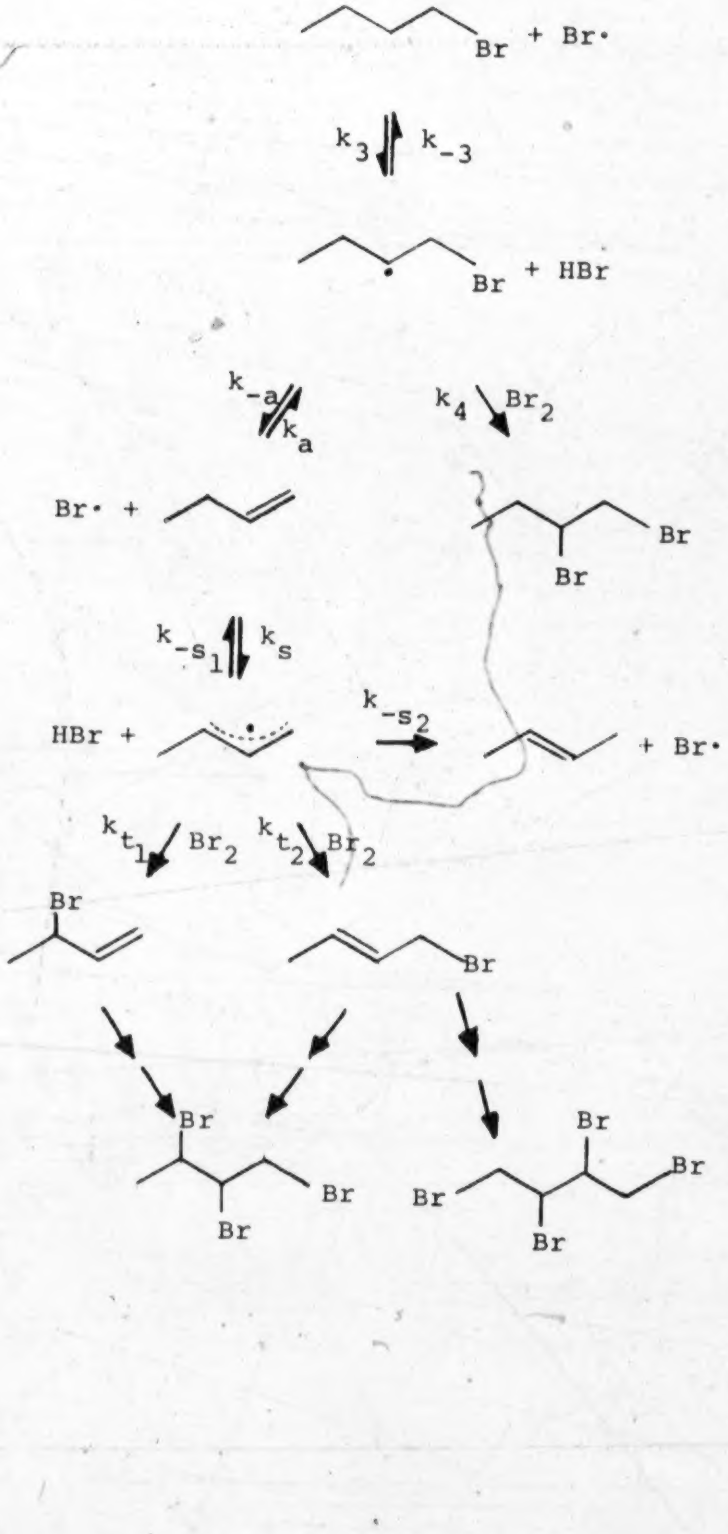
* This interpretation has recently been questioned by Traynham and Lee.[114] These authors pointed out that the relative rates that were most precisely reported showed a three-fold range for the brominating agents used, which was outside the reported uncertainty of the data. They claim that the data actually suggest rather strongly that different hydrogen abstracting radicals were involved in these reactions.

In a preliminary reinvestigation of the vapour phase bromination of 1-bromobutane under "normal" bromination conditions ($BuBr:Br_2 = 5:1$), Tanner and Arhart[103] detected five products at complete consumption of bromine: 1,1-, 1,2- and 1,3-dibromobutane, 1,2,2- and 1,2,3-tribromobutane in a ratio of 0.14:2.36:1.00:0.21:3.43, however, no material balance could be obtained for the bromine consumed, implying that other bromination products were present.

1,2,3-Tribromobutane could have been formed from bromination of either 1,2- or 1,3-dibromobutane (or of both): this was unlikely however, since then the dibromides have to react with bromine much faster than 1-bromobutane. Also, if this were the case, one would expect comparable amounts of tribromide in the liquid phase reaction, unless the rates of bromination were strongly phase dependent. A study of the products of the photobromination of these dibromides in solution and in the gas phase showed that though both compounds gave 1,2,3-tribromobutane, it was a minor product (<6%) in both brominations[103] (see Appendix 4).

A possible mechanism for the formation of 1,2,3-tribromobutane in the vapour phase bromination of 1-bromobutane is given in Scheme 5. In this scheme, the β-bromobutyl radicals are either trapped by bromine or hydrogen bromide or eliminate bromine atoms to give 1-butene. The alkene may then add bromine to form 1,2-dibromobutane or be allylically brominated to give a mixture of 1-bromo-2-butene and 3-bromo-1-butene, which, on addition of bromine, would give 1,2,3-tribromobutane. The allylic bromides may also be allylically brominated and then add bromine to give tetrabromide. 1,2,3,4-Tetrabromobutane was detected by Kharash et al. in the vapour phase photobromination of 1-bromobutane,[109] and, since the completion of this work, in these laboratories. The identification of the tetrabromide and its inclusion as a reaction product constituted a material balance for the reactants used and the products formed (see Appendix 4).

Scheme 5


Br
+ Br·
k_3
k_{-3}
Br
+ HBr
k_{-a}
k_a
k_4
Br_2
Br· +
Br
Br
k_{-s_1}
k_s
k_{-s_2}
HBr +
+ Br·
k_{t_1}
Br_2
k_{t_2}
Br_2
Br
Br
Br
Br
Br
Br
Br
Br
Br

There is ample precedent for elimination from β-bromoalkyl radicals (see section I.2.4). Also, it is well known that allylic bromides are formed in high yields in the bromination of alkenes when the bromine concentration is kept low: this is, after all, the reason for allylic bromination by N-bromosuccinimide, where the NBS serves as a source of a low, steady state concentration of bromine.[116] Molecular bromine itself will brominate alkenes allylically; e.g. Sixma and Riem,[117] and McGrath and Tedder,[118] independently showed that in the liquid phase photobromination of cyclohexene, 3-bromocyclohexene was formed in 84% yield when the bromine was introduced into the solution slowly in a stream of nitrogen.

To determine the importance of elimination in the vapour phase bromination of 1-bromobutane, the reaction with bromine highly enriched in bromine-81 was studied. The vapour phase reactions of 1-butene with bromine and of 1-bromo-2-butene and 3-bromo-1-butene with bromine were also studied to establish if the mechanism proposed in Scheme 5 was reasonable.

II.4.1 Vapour Phase Bromination of 1-Bromobutane with Bromine Enriched in Bromine-81

Two breakseals containing 1-bromobutane (2.25×10^{-3} mol) and bromine (96.04% Br-81, 3.96% Br-79, 3.75×10^{-4} mol) respectively were attached to a 5 l reaction vessel and this was degassed. The two reactants were introduced into the reaction bulb and photolyzed till all the bromine colour was discharged. The contents of the bulb were isolated and the unreacted 1-bromobutane, 1,2-dibromobutane, 1,3-dibromobutane and 1,2,3-tribromobutane were collected by preparative glpc and analyzed by mass spectroscopy (Table 21). The parent peaks were scanned at least five times at 70 and 15 ev. The ratio of the parent peaks was insensitive to the ionization voltage.

1,2,3-Tribromobutane did not give a parent peak under any conditions. The peak with the highest m/e value was the P-Br peak. An attempt was made to obtain a parent peak using chemical ionization with ammonia or methane. This was also unsuccessful and no results on this important tribromide were obtained from this reaction.

1-Bromobutane was found to have the same isotopic ratio of bromine as before reaction (i.e. Br-79:Br-81 = 0.507:0.493); this showed that if elimination to 1-butene were taking place, readdition of hydrogen bromide to the alkene was not detectable. This result is not suprising, however, in lieu of the large amount of 1,2,3,4-tetrabromide that is formed, since only 10% of the starting bromide was converted to bromination product and any change that did take place would be highly attenuated by the unreacted starting material. From the relative peak intensities of the parent peaks of the dibromides, the average Br-79:Br-81 ratio for the two molecules could be determined (see Appendix 3), as well as the isotopic ratio of each bromine atom in these dibromides (see Table 21). Due to the small size of the first peak, m/e 214, the errors in these calculated values were quite large.

For a direct substitution mechanism, the dibromides should both contain 27.3% Br-79 and 72.7% Br-81, while the mass spectral peak intensities should be in a ratio of 1:25:24 (see section I.2.4). The difference between the isotopic content and the mass spectral peak intensities of the dibromides from that of direct substitution showed that the two dibromides

Table 21

Vapour Phase Photobromination of 1-Bromobutane (4.5×10^{-4} M) with Bromine-81 (7.5×10^{-5} M)[a]

Compound	m/e[b] 214	216	218	Total Br-79 : Br-81[c]	Isotopic ratio of Bromine[d] Atom # 1	Atom # 2
1-Bromobutane[e]	-	-	-	50.7 : 49.3±0.3		
1,2-Dibromobutane	1.0	10±2	16±3	22 : 78±2	33 : 67±2	11 : 89±3
1,3-Dibromobutane	1.0	6.6±0.7	5.9±0.7	32 : 68±2	49 : 51±2	15 : 85±2

[a] Bromine was 96.04% Br-81 and 3.96% Br-79; reaction was run at 23°.

[b] Intensities of the molecular ion peaks relative to the peak at m/e 214.

[c] The ratio of Br-79 : Br-81 for the whole molecule.

[d] The isotopic ratio (Br-79 : Br-81) of each of the two bromine atoms in the dibromide, obtained from equation 105, Appendix 3.

[e] Recovered after reaction.

were not formed, at least in part, by the same mechanism.

In the formation of 1,3-dibromobutane, since the radical center was two atoms removed from the bromine substituent, no elimination was possible. Therefore, as this dibromide contained more Br-79 than predicted by direct substitution from the original bromine pool, the bromine pool leading to this substitution product must have been enriched in this isotope during the reaction. This is most readily explained by a process involving the elimination of bromine atoms from the β-bromobutyl radicals formed by abstraction of the β-hydrogens of 1-bromobutane. The eliminated bromine atoms (Br-79:Br-81 = 0.506:0.494) mixed rapidly with the bromine pool[68-74] to increase its Br-79 content. 1,3-Dibromobutane, formed by transfer of the γ-radical with the bromine pool, would then contain the original bromine atom (Br-79:Br-81 = 0.506:0.496) and a second bromine atom richer in Br-79 than that predicted by direct substitution with the original bromine pool. The isotopic ratio of the two bromine atoms in this dibromide substantiated this conclusion (see Table 21). One atom (Br-79:Br-81 = 0.49:0.51 ± 0.02) was within experimental error of the original bromine atom in 1-bromobutane. The second bromine atom, i.e. the one at the 3-position, must have come from the "average" bromine pool. The Br-79:Br-81 ratio of the average bromine pool must therefore have been the same as this atom, viz. 0.15: 0.85 ± 0.02.

1,2-Dibromobutane could have conceivably been formed by three distinguishable processes: by direct substitution from the β-bromobutyl radicals, by addition of bromine to 1-butene, or by a combination of both these paths.* In the first case, it would be expected to have the same isotopic composition as 1,3-dibromobutane, which had to be formed by direct substitution. This is clearly not the case. In the second instance, addition of bromine to 1-butene would introduce identical bromine atoms into the two positions of this product. This cannot have been going on exclusively, since the two bromine atoms were different. 1,2-Dibromobutane must have therefore been formed by both pathways. The bromine atom in the 2-position of this product must have come from the bromine pool, immaterial of the mechanism of formation of this compound.* This bromine atom should therefore have the same isotopic ratio as the bromine atom in the 3-position of 1,3-dibromobutane, if the two dibromides were formed at a constant rate relative to each other. This atom must be the one having the Br-79:Br-81 ratio of 0.11:0.89 ± 0.03 (see Table 21). Although the isotopic composition of this atom was within experimental error of the second bromine atom in 1,3-dibromobutane, the small difference may imply that addition to 1-butene takes place to larger extents at the early stages of the reaction, when the bromine pool was not substantially diluted with bromine-79.

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* A fourth process is also possible: this would involve addition of hydrogen bromide to 1-butene to give 1-bromobutane (not containing the original bromine atom) which would then be brominated to give 1,2-dibromobutane. This path cannot be important since the recovered 1-bromobutane after reaction was not detectably enriched in bromine-81; furthermore, bromination of 1-butene in the vapour phase with with added hydrogen bromide gave only traces of 1-bromobutane (see section II.4.3).

These results were consistent with elimination of bromine atoms from the β-bromobutyl radicals to give 1-butene, and at least part of the alkene added bromine to give 1,2-dibromobutane containing bromine enriched in Br-81 in both the 1- and 2-positions of the molecule. The average fraction of 1,2-dibromobutane that was formed from 1-butene could be calculated if it was assumed that the rate of formation of this dibromide was constant relative to the rate of formation of 1,3-dibromobutane. This fraction was found to be 0.59 (see Appendix 3), showing that on average, more than half of the vicinal dibromide was formed by addition of bromine to 1-butene. This fraction is larger than the corresponding fraction in solution at 40° (section I.2.4). This is reasonable, since elimination in the vapour phase should occur to larger extents than in solution, since the lower concentrations that are normally used in the gas phase reactions make the lifetime of the radicals longer. Elimination of bromine atoms from the β-bromobutyl radicals is a unimolecular reaction, while transfer reactions are necessarily bimolecular: the extent of reaction 62 should therefore depend strongly on the concentration of the transfer agents.

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* An exception to this would be a 1,2-migration of bromine, since this would introduce the original bromine atom of 1-bromobutane into the 2-position. Such a migration is not expected to be important, as it involves the formation of a primary radical from a secondary one. This process, however, if it does occur does not change the isotopic content of the 1,2-dibromobutane formed.

II.4.2 Bromination of 1-Bromobutane in the Vapour Phase

The bromination of 1-bromobutane with bromine under "normal" bromination conditions was studied at different percentage reaction to determine if the product distribution varied with the extent of the reaction. The reactions were run in a 5 l reaction bulb, and after photolysis, the contents of the bulb were collected, an internal standard added, and the residual bromine concentration determined by iodometric titration. The organic compounds were extracted in dichloromethane, and analyzed by glpc. Five products were detected (Table 22), 1,1-, 1,2- and 1,3-dibromobutane, 1,2,2- and 1,2,3-tribromobutane. No tetrabromide was detected in these reactions: 1,2,3,4-tetrabromobutane is a solid and is insoluble in dichloromethane and Freon 113. It was also not eluted from the glpc columns that were used to analyze the products of these bromination reactions. Recently (see Appendix 4) it has been shown that the tetrabromide is formed in these reactions at ambient temperatures. It is probable that it was not detected in the reactions listed in Table 22. The results in this table are therefore listed as the percentage of the products detected. Control experiments showed that recovery from the reaction vessel of all these products was always >97%.

At low conversion of the bromine, the major product detected was 1,2-dibromobutane; as the reaction progressed, however, the amount of this product decreased steadily, while the amount of 1,2,3-tribromobutane (and presumably 1,2,3,4-tetrabromide) increased. These results were consistent with the proposal that 1,2-dibromobutane and 1,2,3-tribromobutane (and 1,2,3,4-tetrabromide) were formed from the same intermediate, which was trapped as dibromide to a large extent when the bromine concentration was high, and which gave increasing amounts of polybromide as the bromine was consumed.

Table 22

Photobromination of 1-Bromobutane (2.6×10^{-4} M) with Molecular Bromine (5.0×10^{-5} M) to Different Percent Conversion in the Vapour Phase at 23°

% Conversion	Products,[a] relative ratios 1,1	1,2	1,3	1,2,2	1,2,3
5	1.2	58.1	15.1	0.0	25.6
12	2.4	52.6	15.4	0.0	29.7
30	2.1	47.3	17.4	1.2	32.0
100	2.0	32.7	14.2	2.9	48.3

[a] Reported as percentage of the sum of the products that were detected.

It appeared likely that if the initial bromine concentration were high enough, and this concentration did not change significantly during the reaction, most of the intermediate would be trapped as dibromide. When 1-bromobutane (8.20×10^{-5} M) was allowed to react with molecular bromine (1.46×10^{-4} M) in the vapour phase to 6% conversion of 1-bromobutane, 1,2,3-tribromobutane made up only 3% of the total products (Table 23, reaction 1), and the major product was 1,2-dibromobutane. Increasing the bromine concentration further did not significantly change the amount of 1,2,3-tribromobutane formed (Table 23, reaction 2).

Thus the presence of large amounts of transfer reagent eliminated most of the tribromide usually formed in the vapour phase photobromination of 1-bromobutane. This may be due to the trapping of β-bromobutyl radicals before they eliminate or due to addition of bromine to the alkene instead of allylic bromination at the high bromine concentrations used. The former is more probable, since bromination of 1-butene in the vapour phase gave large yields of allylic bromination under all conditions used (see section II.4.3). In any case, the formation of 1,2,3-tribromobutane in the gas phase under "normal" bromination conditions is due to the low concentrations that are normally used in the gas phase reactions.

Table 23

Photobromination of 1-Bromobutane Under Special Conditions[a]

Reaction #	$[C_4H_9Br]°$	$[Br_2]°$	% Conversion[b]	Products, %[c] 1,1	1,2	1,3	1,2,3
1[e,d]	0.82	1.46	6	2.1	79.1	16.0	2.9
2[f,d]	0.45	47.1	14	1.7	79.6	17.0	1.7
3[g,d]	3.14	11.5	16	1.7	81.9	13.1	3.3
4[h]	2.78	0.66	100	0.4	34.4	23.2	42.0

[a] Concentrations M, x 10^4.

[b] Percent conversion based on 1-bromobutane, except for reaction 4, where it is based on bromine.

[c] Products were identified by collection and comparing their nmr and mass spectra with those of the authentic materials.

[d] The 1,2,3,4-tetrabromobutane is omitted from the material balance and presumably it is formed in amounts approximately equal to that of 1,2,3-tribromobutane (see Appendix 4).

[e] Gas phase, 12 l reaction bulb, 22°.

[f] Gas phase, 5 l reaction bulb, 24°.

[g] Gas phase, 12 l reaction bulb, 23°. This reaction was 4.82 x 10^{-3} M in hydrogen bromide.

[h] Freon 113, 3 l, 26°, this reaction gives a 97.7% material balance based on bromine.

On the basis of this argument, the gas phase distribution of products should be obtained in solution if low enough concentrations of molecular bromine were used. A Freon 113 bromination was run (Table 23, reaction 4) using the same concentrations as in the vapour phase reactions (cf. Table 22). The solution was photolyzed till all the bromine colour was discharged, a known amount of two internal standards was added, and the solution was washed with aqueous sodium bisulphite solution and dried. It was carefully concentrated by distillation on a spinning band column and then analyzed by glpc.

The ratio of the two internal standards (chlorobenzene and o-dichlorobenzene) was the same before and after the distillation, showing that no loss of the lower boiling products took place during the distillation. Only four products were detected, and their relative yields were very similar to those obtained in the vapour phase reaction under "normal" bromination conditions. In contrast to the usual liquid phase brominations, the major product was 1,2,3-tribromobutane (42%), as expected from the reaction of bromine with 1-butene under these conditions, i.e. allylic bromination rather than addition. In the solution phase reaction no allylic bromination of the bromobutenes seems to have taken place since a material balance was obtained (i.e., no 1,2,3,4-tetrabromobutane was formed).

In view of these results, Tedder's recent report on the reaction of 1-bromobutane with bromine in a static system in the gas phase is surprizing. In his original study, using a flow system, no 1,2-dibromobutane was detected, and a brown film, probably due to polybromides, formed on the surface of the reaction vessel.[13] In his reinvestigation of the reaction in a static system (see Table 20), no polybromides were reported.[82] In this case, after photolysis, the reaction mixture was passed through a "Carbosorb" (soda lime) column to separate the unreacted bromine and hydrogen bromide from the organic materials. The ratio of 1,2- to 1,3-dibromobutane that was reported at high conversion of bromine (2.2, 100°) is the same as that reported by Kharasch et al. (2.2, 100°)[109] and that found in this study (2.3, 23°, cf. Table 22, last reaction) at complete conversion of the bromine. It is possible that the polybromides that were formed in Tedder's reaction were trapped in the Carbosorb column and therefore could not be detected in the subsequent glpc analyses.

These results gave strong support to the mechanism proposed in Scheme 5 for the formation of 1,2,3-tribromobutane and 1,2,3,4-tetrabromobutane in the gas phase. In solution, in the presence of a high concentration of bromine the 1-butene that is formed by elimination of bromine atoms from the β-bromobutyl radicals adds bromine (ionically and/or free radically) to give 1,2-dibromobutane exclusively. When the concentration of bromine is low, either in the gas phase or in solution, the butene is brominated allylically and the allylic bromides add bromine to give 1,2,3,4-tetrabromobutane and/or 1,2,3-tribromobutane. On the basis of the bromination with Br-81 in the vapour phase, however, part of the butene adds bromine, even in the gas phase.

II.4.3 Bromination of 1-Butene in the Vapour Phase

A study of the vapour phase photobromination of 1-butene was undertaken to obtain more evidence for the mechanism proposed in Scheme 5 (page 127). From the proposed mechanism, the rate of formation of substitution products relative to the rate of formation of addition product from 1-butene is given by equation 68, where $k_t = k_{t_1} + k_{t_2}$ (Scheme 5).

$$\frac{d(\text{Substitution})/dt}{d(\text{Addition})/dt} = \frac{k_t[A\cdot]}{k_4[R\cdot]} \qquad (68)$$

Assuming a steady state concentration of 2-bromobutyl (R·) and allylic (A·) radicals, this expression may be rewritten to eliminate these species (equation 69), where

$$\frac{d(\text{Substitution})/dt}{d(\text{Addition})/dt} = \frac{k_t k_s (k_{-a} + k_4[\text{Br}_2])}{k_4 k_a (k_{-s}[\text{HBr}] + k_t[\text{Br}_2])} \qquad (69)$$

$k_{-s} = k_{-s_1} + k_{-s_2}$. The rate of substitution relative to the rate of addition is therefore independent of the alkene concentration, but dependent on the bromine and hydrogen bromide concentrations.

The bromination of 1-butene with molecular bromine was run in the vapour phase under different conditions (Table 24). Only four products were detected when the reaction was run with an excess of 1-butene: 1-bromobutane, 1-bromo-2-butene, 3-bromo-1-butene and 1,2-dibromobutane. The products were identified by comparing their glpc retention times with those of authentic materials. They were also collected by preparative glpc and the mass and nmr spectra were identical with those of the authentic compounds (see section III.12). Only a trace of 1-bromobutane was detected in all the reactions (<0.4%); it is not included among the products in Table 24.

2-Butene was never detected in these reactions.

Table 24

Vapour Phase Photobromination of 1-Butene with Molecular Bromine

Reaction #	$[C_4H_8]^a$	$[Br_2]^a$	Vol., ℓ	Equil. Time[b]	Products, %[c]		
					1	2	3
1	2.25	0.46	5	0	28.4	67.4	4.2
2	49.4	11.9	5	0	18.6	41.9	39.5
3	10.7	2.37	5	2	16.9	42.8	40.3
4	0.16	0.03	5	3	25.8	64.4	9.8
5	1.65	0.31	5	12	23.6	56.8	19.7
6	1.61	0.34	5	20	17.1	43.2	39.6
7	0.67	0.13	12	20	27.2	65.1	7.7
8	0.38	0.07	22	5	30.1	67.4	2.5
9	0.31	0.03	22	24	23.4	68.4	3.2
10	2.72	0.51	22	0	26.2	69.2	4.2
11[d]	0.49	0.07	22	0	25.3	71.7	3.0

continued .....

Table 24 (cont'd.)

[a] Concentrations M, x 10^4. All reactions were run at 27°, except reactions 8 and 9, which were run at 23°.

[b] Time (minutes) reactants were left to equilibrate in the absence of light prior to irradiation.

[c] Only four products were detected, 3-bromo-1-butene (1), 1-bromo-2-butene (2), 1,2-dibromobutane (3) and 1-bromobutane. The latter always made up less than 0.4% of the products and is not reported in the results in this Table.

[d] This reaction was 7 x 10^{-7} M in hydrogen bromide.

In order to optimize the conditions for its formation, 1-butene was brominated in the presence of equimolar amounts of bromine and hydrogen bromide (reaction 11, Table 24). No 2-butene was formed in this reaction either. 2-Butene should be the major product from reaction of the allylic radical with hydrogen bromide, and the large excess of 1-butene in this reaction should ensure that any 2-butene that is formed would not be completely brominated. The absence of this isomer in these reactions indicates that reversal with hydrogen bromide does not compete effectively with transfer with bromine, and therefore equation 69 may be simplified to equation 70, which predicts that rate of allylic substitution relative to the rate of addition to 1-butene should increase as the bromine concentration is decreased.

$$\frac{d(\text{Substitution})/dt}{d(\text{Addition})/dt} = \frac{k_s}{k_a}\left(1 + \frac{k_{-a}}{k_4[\mathrm{Br}_2]}\right) \qquad (70)$$

A large yield of the two allylic bromides was always formed in the vapour phase photobromination of 1-butene, together with variable amounts of 1,2-dibromobutane. The yield of the addition product was found to depend on the concentration of molecular bromine (cf., e.g., reactions 1 and 2, Table 24), as expected, on the time the two reactants were left to equilibrate in the absence of light prior to the photolysis (cf. reactions 1, 5 and 6, Table 24), and on the size of the reaction bulb (cf. reactions 4, 8 and 9, Table 24). The last two observations indicated that the dibromide was probably formed at least in part by an ionic addition of bromine to 1-butene on the surface of the reaction vessel. When very low concentrations of bromine were used in a 22 l reaction bulb, 1-butene gave up to 97.5% yield of the two allylic bromides, and the amount of 1,2-dibromobutane did not increase significantly by increasing the equilibration time (cf. reactions 8 and 9, Table 24). The large yield of allylic bromides is probably due to the reversibility of the addition reaction, i.e. k_{-a} in equation 70.

1,2,3-Tribromobutane was not detected in the brominations of 1-butene with a deficiency of molecular bromine: the alkene was therefore brominated allylically much faster than the allylic bromides added bromine to give tribromide. Since in the bromination of 1-bromobutane allylic bromides were not detected, the allylic bromides must have added bromine faster than 1-bromobutane brominated. To substantiate this proposal, a mixture of 1-bromo-2-butene and 3-bromo-1-butene (6.7×10^{-5} M) and 1-bromobutane (6.2×10^{-5} M) was allowed to react with bromine (5.70×10^{-5} M) in the vapour phase.

Three products were detected by glpc, 1,2- and 1,3-dibromobutane and 1,2,3-tribromobutane. Assuming that the dibromides were formed from the bromination of 1-bromobutane, the relative rate of bromination of the allylic bromides to that of 1-bromobutane was calculated to be 53 (see section III.13). Since tetrabromide was undoubtedly formed in this reaction, and was not detected in the analysis, this relative rate must be taken as a minimum. (Since the completion of this work the 1,2,3,4-tetrabromobutane has been detected in this reaction).

Since the major products (polybrominated butanes) in the competitive bromination must have been formed from the allylic bromides, this experiment showed that the allylic bromides did in fact give 1,2,3-tribromobutane and 1,2,3,4-tetrabromobutane on reaction with bromine in the vapour phase at ambient temperature. In a separate experiment to test this, the bromination of 1-butene (3.60×10^{-6} M) with excess bromine (8.6×10^{-5} M) in the vapour phase was studied. The mixture was photolyzed for five seconds, and then a large excess of toluene (5.3×10^{-4} M) was introduced and the system irradiated till all the bromine had reacted. The products were collected and analyzed by glpc. Only three products were detected, benzyl bromide (95.8% based on bromine), 1,2-dibromobutane (0.4%) and 1,2,3-tribromobutane (3.5%). This result gave further proof that 1,2,3-tribromobutane was formed from 1-butene in the bromination of 1-bromobutane.

1,2,3,4-Tetrabromobutane was not observed in these brominations, or those of 1-bromobutane (section II.4.2). It may have been formed and not detected. The work-up of the reaction mixtures included drying over magnesium sulphate or the addition of solid sodium hydrogen carbonate to the frozen mixture. Since this tetrabromide is a solid, it might have been lost in these steps. Its formation in these reactions, however, should not effect any of the arguments presented here; it would only indicate that the allylic bromides may be brominating allylically as well as adding bromine to give 1,2,3-tribromobutane.

II.4.4 Kinetic Study of the Bromination of Perdeuterio-1-bromobutane in the Vapour Phase

The reaction of the β-bromobutyl radicals other than transfer with bromine and with hydrogen bromide in the vapour phase leads partly to 1,2,3-tribromobutane through the formation of 1-butene. The extent of this reaction may therefore be monitored by the amount of 1,2,3-tribromobutane produced in the bromination of 1-bromobutane in the vapour phase. Since when this reaction was carried out in the presence of excess molecular bromine and excess hydrogen bromide in the vapour phase, <4% of this tribromide was formed (see reaction 3, Table 23), it was anticipated that the the bromination of perdeuterio-1-bromobutane under these conditions would be only minimally complicated by elimination from the perdeuterio-β-bromobutyl radicals. The relative rates of abstraction from perdeuterio-1-bromobutane by bromine atoms, and the relative rates of transfer of the isomeric perdeuterio-bromobutyl radicals with bromine and with hydrogen bromide could be determined using the same method as was used for perdeuterio-1-chlorobutane (section II.3.1).

Under these conditions (excess bromine and excess hydrogen bromide, 12 or 22 l reaction vessels, see Table 25), six products were detected other than unreacted starting material when the recovered reaction mixture was analyzed by glpc: 1,1-, 1,2- and 1,3-dibromobutane-d_8, 1,2,2-, 1,3,3- and 1,2,3-tribromobutane-d_7. These products were identified by comparison of their glpc retention times with those of the authentic, non-deuterated materials on two columns. They were collected by preparative glpc and their mass spectra were found to be identical with those of the protiated compounds when they were corrected for the presence of deuterium instead of protium.

The yield of 1,2,3-tribromobutane-d_7 was

Table 25

Photobromination of Perdeuterio-1-Bromobutane with Excess Bromine and Excess Hydrogen Bromide in the Vapour Phase

	Concentration M, x 10^5			
	1^a	2^a	3^b	4^b
Reactants[c]				
$[RD(H)]°$	23.36	44.58	16.40	15.56
$[Br_2]°$	83.83	144.13	83.35	83.89
$[HBr]°$	364.8	596.0	865.5	842.6
$[R^{\alpha}H]°$	1.51	2.88	1.06	1.01
$[R^{\beta}H]°$	0.26	0.50	0.18	0.18
$[R^{\gamma}H]°$	0.48	0.92	0.34	0.32
$[R^{\delta}H]°$	1.88	3.59	1.32	1.25
Products				
$[RD(H)]$	16.03	38.32	14.76	11.33
$[R^{\alpha}H]$	1.54	2.92	1.07	1.03
$[R^{\beta}H]$	0.72	0.96	0.28	0.66
$[R^{\gamma}H]$	1.01	1.58	0.42	0.70
$[R^{\delta}H]$	1.91	3.61	1.33	1.26
$[R^{\alpha}Br]$	0.11	0.15	0.02	0.05
$[R^{\beta}Br]$	5.25	5.98	0.50	2.33
$[R^{\gamma}Br]$	0.78	0.97	0.05	0.24
$[R^{\delta}Br]$[d]	0.00	0.00	0.00	0.00
1,2,3-Tribromide[e]	0.14	0.09	0.00	0.06
Other[f]	0.14	0.15	0.00	0.05

continued......

Table 25 (cont'd.)

	1^a	2^a	3^b	4^b	Average
Relative Rate Constants[g]					
k_{Br_2}/k_{HBr}[h]	26.2	26.6	29.6	30.2	28.2±1.8
k_2/k_{-1}	16.4	15.5	17.0	25.1	18.5±3.3
k_4/k_{-3}	52.3	55.9	51.9	51.1	52.8±1.6
k_6/k_{-5}	6.40	6.08	6.49	6.34	6.33±0.14
k_1/k_5	0.11	0.12	0.20	0.11	0.13±0.03
k_3/k_5	4.57	4.10	4.62	4.71	4.50±0.20
k_7/k_5	0.01	0.01	0.05	0.01	0.02±0.01
Temperature	24°	26°	24°	25°	

[a] Run in 12 l reaction vessel.

[b] Run in 22 l reaction vessel.

[c] [RD(H)] refers to the concentration of perdeuterio-1-bromobutane, and $[R^1H]$ is the average concentration of protium at position 1.

[d] Not detected by glpc.

[e] 1,2,3-Tribromobutane.

[f] 1,2,2-Tribromobutane (~95%) and 1,3,3-tribromobutane (~5%).

[g] See Scheme 1. Calculated using equations 23 or 29.

[h] Relative rate of transfer of perdeuteriobromobutyl radicals with bromine and with hydrogen bromide.

always less than 2% of all the bromination products. Therefore only about 2-4% (corrected for undetected 1,2,3,4-tetrabromobutane) elimination was taking place, since only negligible amounts of 1,2,3-tribromobutane come from the bromination of other products (see Appendix 4). Only traces of 1,3,3-tribromobutane-d_7 were detected; this compound is the major bromination product of 1,3-dibromobutane-d_8 (see Appendix 4). The material balance in these brominations, based on perdeuterio-1-bromobutane, was always greater than 91%. Control experiments on the recovery and isolation procedures, using mixtures of 1-bromobutane, 1,2-, 1,3- and 1,4-dibromobutane, 1,2-3-tribromobutane, molecular bromine and hydrogen bromide (see section III.4), showed that the yield of the recovered dibromides was greater than 98%, and that of the tribromide was greater than 97%.

The unbrominated perdeuterio-1-bromobutane was collected by preparative glpc and the amount of protium incorporation at each position was determined from a comparison of the H^1 100 MHz spectrum of the residual protium in the starting material and the spectrum of the recovered perdeuterio-1-bromobutane (Table 25), using 1,1-diphenylethene as internal standard (see Fig. 7 and 8).

The relative rates of transfer of the bromo-

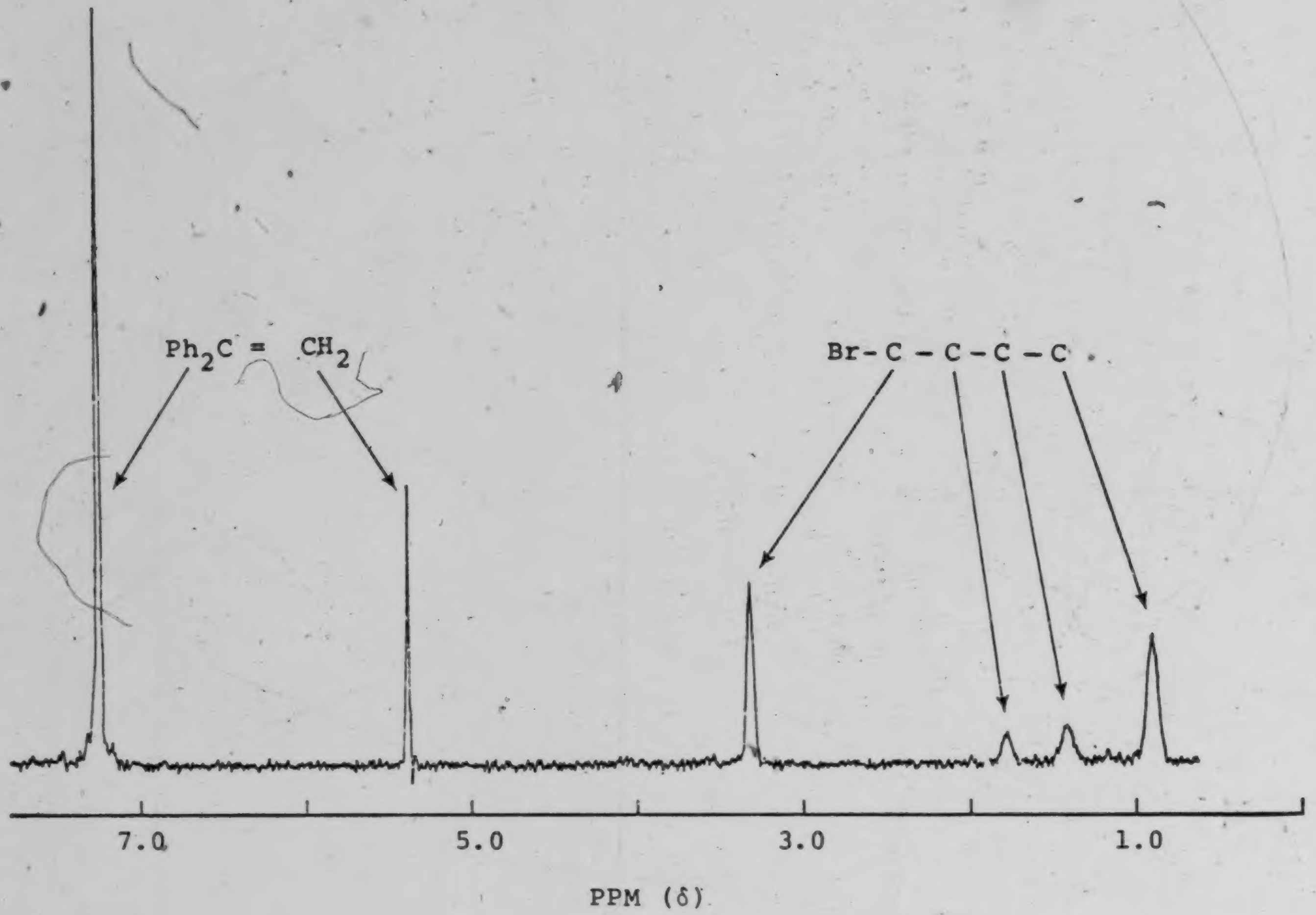


Fig. 7. NMR Spectrum of a Freon 113 Solution of Perdeuterio-1-bromobutane (after reaction) and 1,1-Diphenylethene (TMS internal standard)

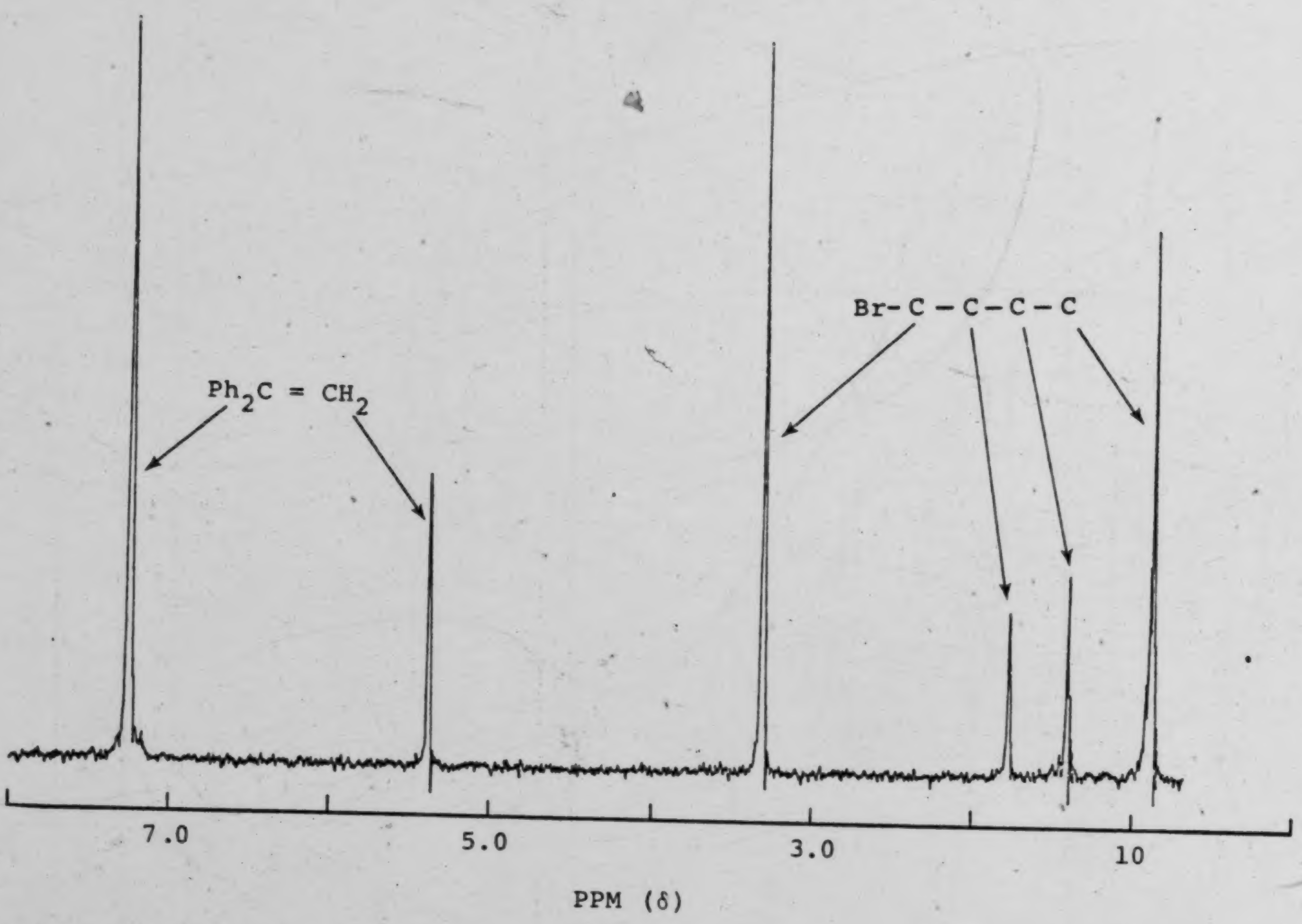


Fig. 8. Deuterium Decoupled NMR Spectrum of a Freon 113 Solution of Perdeuterio-1-bromobutane (after reaction) and 1,1-Diphenylethene (TMS internal standard)

butyl radicals with bromine and with hydrogen bromide were determined using equation 23; they were found to be independent of the ratio of bromine to hydrogen bromide and of the volume of the reaction vessel (Table 25). The relative rate of transfer for the bromobutyl radicals with bromine and with hydrogen bromide was calculated as 28.2 ± 1.4. Thus only 3.4% of the radicals formed reverse with hydrogen bromide when the concentrations of bromine and hydrogen bromide are equal. 1-Bromobutane is therefore more deactivated towards reversal than 1-chlorobutane is, where 7.5% of the radicals formed reversed with hydrogen bromide under these conditions (section II.3.1).

The relative rates of transfer for the isomeric bromobutyl radicals were 18.5 ± 3.3, 52.8 ± 1.6 and 6.33 ± 0.14 for the α-, β- and γ-radicals respectively. The relative rate of transfer with bromine and with hydrogen bromide for the δ-position could not be calculated, as no perdeuterio-1,4-dibromobutane was detected. Assuming that ~~a~~ concentration of 10^{-8} M of this compound would have been detected by glpc, k_8/k_{-7} (Scheme 1, X = Br) must be less than 0.2. The rates of deuterium abstraction from perdeuterio-1-bromobutane, relative to the rate of abstraction of the γ-deuterium, obtained using equation 29, were 0.13 ± 0.03, 4.50 ± 0.20 and

0.02 ± 0.01 for the α-, β- and δ-positions respectively.

The β-position is clearly unique in the molecule. The relative rates of transfer with bromine and with hydrogen bromide for the γ- and δ-radicals are very similar to those for the analogous radicals from perdeuterio-1-chlorobutane (cf. Table 14); the ones for the perdeuteriochlorobutyl radicals are slightly larger, as expected from the greater polar effect of the chlorine substituent (this assumes that the rate of transfer with molecular bromine is the same for analogous chloro- and bromoperdeuteriobutyl radicals). The α-radical in perdeuterio-1-chlorobutane is much more deactivated towards reversal than that radical from perdeuterio-1-bromobutane. This is also expected, since the α-position is the position that suffers the largest inductive polar deactivating effect. The relative rate of abstraction of the α-deuterium relative to the γ-deuterium is larger for perdeuterio-1-chlorobutane ($k_1/k_5 = 0.34$) than for its bromo-counterpart ($k_1/k_5 = 0.13$); probably, this reflects the weaker C-D bond in the former compound, and the greater stabilization of the radical in the transition state by chlorine (structure **2b**, page 4).

The β-position of perdeuterio-1-bromobutane is unique towards reversal and abstraction. The rate of transfer with bromine relative to that with hydrogen bromide of the β-bromobutyl radicals ($k_4/k_{-3} = 53$) is more than three times bigger than that for the more deactivated, β-chlorobutyl radicals ($k_4/k_{-3} = 16$). The relative rate of transfer is, in fact, quite similar to that for the α-chlorobutyl radicals. These results indicate that the C-D bonds β to the bromine substituent are weaker than expected. The weaker bond strength is also indicated by the relative rate of abstraction of the β- and γ-deuteriums, $k_3/k_5 = 4.5$. Assuming that the polar effects for a chlorine and a bromine substituent are roughly the same on the γ-position, then the deuterium β to the bromine substituent is abstracted ~ 9 times faster than that β to the chlorine substituent.

II.4.5 Bromination of 1-Bromobutane in the Vapour Phase

The relative rates of hydrogen abstraction from 1-bromobutane may be obtained from the bromination of this compound under conditions where reversal and elimination were negligible, e.g. in the reaction with excess bromine run to low conversion of 1-bromobutane (reactions 1 and 2, Table 23).

Table 26

Comparison of the Relative Rates of Abstraction from 1-Bromobutane by Bromine Atoms in the Vapour Phase

Method[a]	k_1/k_5[b]	k_3/k_5[b]
Kinetic data from Perdeuterio-1-bromobutane (Table 25)	0.13	4.50
Bromination of 1-bromobutane, 0.6:1.0, 6% conversion (reaction 1, Table 23)	0.13	5.13
Bromination of 1-bromobutane, 0.01:1.0, 14% conversion (reaction 2, Table 23)	0.10	4.78

[a] Ratio given is that of 1-bromobutane:bromine.

[b] The average of the results for 1-bromobutane (last two entries of the table) is 0.12 ± 0.02 for k_1/k_5, and 4.95 ± 0.18 for k_3/k_5.

These results are given in Table 26, where they are compared to the results obtained from perdeuterio-1-bromobutane. The rates of abstraction of the α- and β-hydrogens relative to the rate of abstraction of the γ-hydrogens were 0.12 ± 0.02 and 4.95 ± 0.18 respectively.

Both these results are in reasonable agreement with those obtained from the kinetic study of perdeuterio-1-bromobutane, and indicate that deuterium isotope effects are unimportant in these relative rates of abstraction.

These results compare very well with the result obtained by Traynham for the bromination of 1-bromobutane in liquid bromine at 60°. On the basis of the results obtained from cyclohexane and 1-chlorobutane, the relative rates of abstraction in liquid bromine should not be complicated by cage, complex or solvent effects, and should be the same as in the gas phase in the absence of reversal. Traynham reports that the ratio of 1,2- to 1,3-dibromobutane was 5.1,[114] which is the same as found in the bromination of 1-bromobutane in the gas phase with excess bromine (Table 23), and very close to the result obtained from perdeuterio-1-bromobutane.

Since the mechanism proposed in Scheme 1 (X = Br) was not applicable to the vapour phase bromination of 1-bromobutane under "normal" bromination conditions because of the elimination of bromine atoms from the β-bromobutyl radicals, a test for the kinetic data similar to the one applied for the bromination of 1-chlorobutane (section II.3.2) could not be performed. Instead, 1-bromobutane was brominated with excess bromine and excess hydrogen bromide in the vapour phase. The products were isolated, and the ratio of the products relative to 1,3-dibromobutane determined by glpc. (Table 27). 1,2,3-Tribromobutane made up <3% of all the products in these reactions, indicating that there was only minimal complication from the elimination reaction under these conditions.

The ratio of the rates of formation of any two products is given by equation 24 (section II.1). Under the conditions of these brominations (i.e. when the bromine and hydrogen bromide concentrations do not change significantly during the reaction), this equation may be integrated (equation 71). Equation 71 may be used to predict the ratio of 1,1- to 1,3-dibromobutane,

$$\frac{[R^{\alpha}Br]}{[R^{\gamma}Br]} = \frac{k_1}{k_5}\left(\frac{k_{-5}/k_6 + [Br_2]/[HBr]}{k_{-1}/k_2 + [Br_2]/[HBr]}\right) \qquad (71)$$

Table 27

Vapour Phase (22 1) Photobromination of 1-Bromobutane with Excess Bromine and Excess Hydrogen Bromide[a]

$[C_4H_9Br]°$	$[Br_2]°$	[HBr]°	% Reaction[b]	$R^{\alpha}Br/R^{\gamma}Br$[c]		$R^{\beta}Br/R^{\gamma}Br$[d]	
				Observed	Calculated[e]	Observed	Calculated[e]
3.138[f]	11.47	48.16	16	0.13±0.01	0.18±0.05	6.52±0.21	6.93±0.39
1.497	8.773	39.94	16	0.16±0.01	0.18±0.05	7.20±0.29	7.12±0.41
1.393	3.196	24.31	3	0.15±0.01	0.20±0.06	8.52±0.25	8.66±0.53
1.751[g]	8.754	85.96	15	0.24±0.01	0.22±0.06	9.98±0.[illegible]1	9.68±0.68
1.657	7.950	99.27	31	0.16±0.01	0.23±0.07	10.89±0.45	10.82±0.71

[a] All concentrations M, x 10^4; reactions run at 23±1°.

[b] Based on 1-bromobutane.

[c] Ratio 1,1- to 1,3-dibromobutane.

[d] Ratio of products from attack at the 2-position (1,2-dibromobutane, 1,2,2- and 1,2,3-tribromobutane) to 1,3-dibromobutane. 1,2,3-Tribromobutane was always <3% of the total products.

continued.....

Table 27 (cont'd.)

[e] Calculated from equation 71, using the relative rate data of Table 25.

[f] Run in a 12 l reaction bulb.

[g] Perdeuterio-1-bromobutane was used in this reaction.

and similar expression can be derived for the 1,2- to 1,3-dibromobutane ratio. The calculated ratios were computed using the relative rate data obtained from perdeuterio-1-bromobutane (Table 25), and are compared to the observed ratios in Table 27.

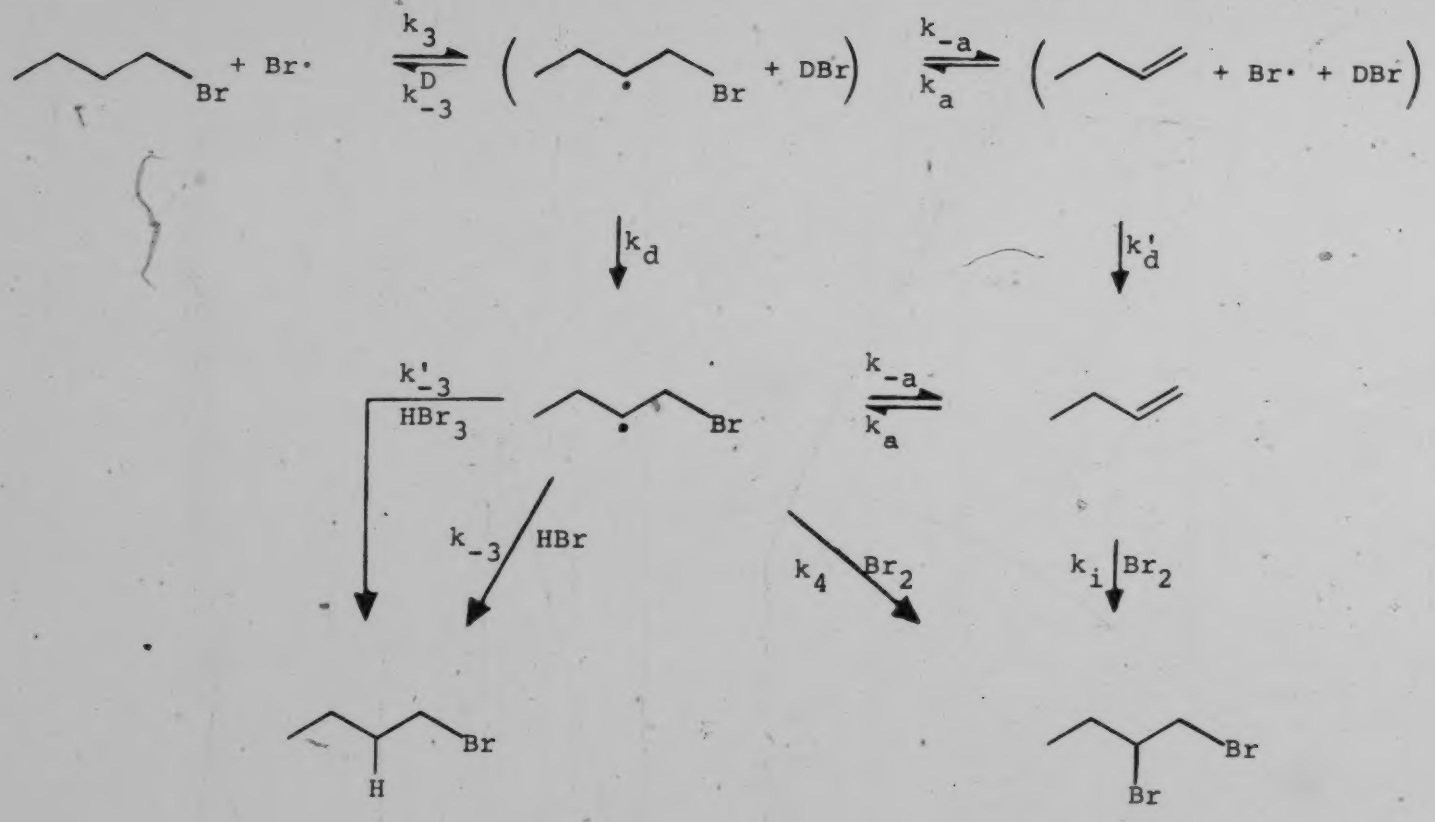
The error limits in the calculated ratios were obtained using the maximum and minimum values of the relative rates reported in Table 25, while the errors in the observed ratios are glpc errors (± 2%). The calculated and observed values coincide for all the five reactions of Table 27; this coincidence shows that the relative rate data obtained for perdeuterio-1-bromobutane describes well the bromination of 1-bromobutane, and again shows that the assumption made in equation 30 (section II.1) was valid.

II.4.6 Comparison of Liquid and Vapour Phase Results

The bromination of perdeuterio-1-bromobutane in Freon 113 solution with excess bromine and excess hydrogen bromide has also been studied in these laboratories.[119] The mechanism proposed in Scheme 4 for the bromination of 1-chlorobutane in solution should be applicable to the bromination of 1-bromobutane and perdeuterio-1-bromobutane at the α-, γ-, and δ-positions in the liquid phase, since the radicals derived from these positions cannot form olefin. However, a modified mechanism must be considered for bromination at the 2-position (Scheme 6).

In this mechanism, abstraction of deuterium from the 2-position leads to a caged β-bromobutyl radical-deuterium bromide pair. The β-bromobutyl radical radical may reverse with the caged deuterium bromide, or it may diffuse out of the cage. The "free" β-bromobutyl radical may be trapped with bromine, hydrogen bromide or hydrogen tribromide. This radical may also eliminate a bromine atom to form 1-butene, which may add bromine ionically to give 1,2-dibromobutane or add a bromine atom to give back β-bromobutyl radicals. On the basis of the results from the liquid phase bromination of 1-bromobutane with bromine-81 (section I.2.4), a substantial amount of elimination takes place in solution. These results indicated that the elimination reaction was competitive with transfer with molecular bromine. Since the latter reaction is competitive with diffusion (section I.2.2), then elimination of bromine atoms from the caged β-bromobutyl radicals may also be competitive with diffusion from the cage (Scheme 6). Readdition in the cage can also conceivably be competitive with diffusion. In the bromination of optically active 2-

Scheme 6


+ Br·
Br
k_3
k^D_{-3}
+ DBr
k_{-a}
k_a
+ Br· + DBr
k_d
k'_d
k'_{-3}
HBr_3
k_{-3}
HBr
k_4
Br_2
k_i
Br_2
H
Br

bromobutane, the racemization in the 2,3-dibromobutane that was formed was greater than that predicted from the large amount of elimination-readdition that was detected by bromination with bromine-81. It was postulated that this may be due to a 1,2-bromine migration in the 3-bromo-2-butyl radicals or due to a cage elimination-readditon mechanism.[64]

This mechanism proved too complicated to be analyzed kinetically, since the rate constants k_a, k_{-a} and k_i could not be determined readily, and the incursion of a second cage, that incorporating 1-butene, a bromine atom and deuterium bromide, makes the comparison of the rates of abstraction impossible in solution. As a result, no values for the relative rates at this positon could be obtained.

For the α- and γ-radicals, the relative rate of transfer with hydrogen tribromide and with hydrogen bromide in solution could be calculated if it were assumed that there were no solvent effects on the relative rate of transfer of these radicals with bromine and with hydrogen bromide (cf. section II.3.3). The cage effects for these two positions could also be calculated in the same way as used for perdeuterio-1-chlorobutane (section II.3.3). The results are given in Table 28.

Table 28

Photobromination of Perdeuterio-1-bromobutane with Excess Bromine and Excess Hydrogen Bromide in Freon 113[a]

	Concentration M, x 10^5			
	1	2	3	Average
Reactants[b]				
$[RD(H)]°$	750	490	344	
$[Br_2]°$	3730	4900	463	
$[HBr]°$	7500	7400	10300	
Products[c]				
$\Delta[R^{\alpha}H]$	2.78	1.12	1.00	
$\Delta[R^{\beta}H]$	11.3	5.29	25.0	
$\Delta[R^{\gamma}H]$	7.25	5.04	4.36	
$\Delta[R^{\delta}H]$	1.83	-	0.61	
$[R^{\alpha}Br]$	3.75	0.795	0.378	
$[R^{\beta}Br]$	129	85.4	40.4	
$[R^{\gamma}Br]$	12.0	6.96	0.765	
$[R^{\delta}Br]$[d]	0.00	0.00	0.00	
Relative Rates[e]				
k'_{-1}/k_{-1}	59.6	132	72.3	88±29
k'_{-5}/k_{-5}	8.4	16.0	26.1	17.0±6.1
Cage Effect				
C^{α}_{γ}	0.38	0.81	0.48	0.61±0.24
C^{γ}_{γ}	1.00	1.00	1.00	1.00

continued.....

Table 28 (cont'd.)

[a] Taken from ref. 119; all reactions were run at 30.0 ± 0.1°.

[b] $[RD(H)]^\circ$ refers to the initial concentration of perdeuterio-1-bromobutane.

[c] $\Delta[R^iH]$ is the increase in protium content at position i.

[d] Not detected by glpc.

[e] Relative rates of transfer with hydrogen tribromide and with hydrogen bromide for the α- (k'_{-1}/k_{-1}) and γ-radicals (k'_{-5}/k_{-5}).

In the calculations of the relative rates of transfer with hydrogen tribromide and hydrogen bromide, and those of the cage effect, it was assumed that any temperature effects on the relative rates were not important over the 5° temperature range between the vapour and solution phase reactions (25° vs 30°). The relative rate of transfer of the γ-perdeuteriobromobutyl radicals with hydrogen tribromide and with hydrogen bromide (17 ± 6) was very close to the analogous rate ratio for the γ-perdeuteriochlorobutyl radicals (27 ± 2) and for the perdeuteriocyclohexyl radicals (22 ± 7), as expected, since these radicals should be very similar. The analogous relative rate for the α-perdeuteriobromobutyl radicals was quite erratic: this probably reflects the large errors involved in measuring the small (<2%) amount of perdeuterio-1,1-dibromobutane formed in these reactions and the equally small amount of protium incorporated at this position.

The cage effect C_{γ}^{α} was calculated as 0.6 ± 0.2, indicating that cage filtering of the γ-perdeuteriobromobutyl radicals was more important than for the deactivated α-perdeuteriobromobutyl radicals. This is not unreasonable, since if one assumes that transfer with bromine of these two radicals is not much influenced by polar effects, the vapour phase results indicate that $k^D_{-1} < k^D_{-5}$, and therefore cage reversal of the α-radicals will be less important than that for the γ-radicals.

II.5 Enhanced Rate of Abstraction in the Bromination of 1-Chlorobutane and 1-Bromobutane

The results obtained for the vapour phase bromination of 1-bromobutane (Table 26) and perdeuterio-1-bromobutane (Talbe 25) indicate that the rate of abstraction of the β-hydrogens or deuteriums is enhanced, and this enhancement overcomes the polar deactivation at the β-position.

The rate of abstraction of the β-deuterium relative to the γ-deuterium from perdeuterio-1-chlorobutane was determined to be 0.49 (Table 14); the corresponding rate for the protiated compound is the same (Table 15). The polar effect thus still regulates the rate of abstraction of the β-hydrogen or deuterium. It is unlikely that there is any rate enhancement in the rate of abstraction of this hydrogen by bromine atoms since the rate of attack on the β-hydrogens of 1-chlorobutane relative to that on the γ-hydrogens is very similar to that reported for other, less selective hydrogen abstracting agents. For example, chlorination of 1-chlorobutane with different reagents gives the following results for k_3/k_5 (Scheme 4): 0.52 (Cl_2, gas phase, 35°),[13] 0.56 (Cl_2, gas phase, 78°),[13] 0.48 (Cl_2, liquid phase, 35°),[66] 0.47 (SO_2Cl_2, liquid phase, 70°),[120] 0.45 (tert-BuOCl, liquid phase, 40°),[121] 0.37 (Cl_2O, liquid phase, 40°),[122] 0.34 ($PhICl_2$, liquid phase, 40°).[123] Furthermore, the relative rate of abstraction of these two hydrogens by bromine atoms is similar to the relative rate of abstraction of the β- and γ-hydrogens from other electronegatively substituted butanes by bromine atoms and by other hydrogen abstracting species (see e.g. Table 1).

For the bromination of 1-bromobutane, an estimate of the polar effect at the β-position is required to determine the magnitude of the enhancement. If it is assumed that the polar effect is the same for a chlorine and a bromine substituent (probably a chlorine substituent exerts a larger polar effect, cf. Tables 14 and 25), then the rate enhancement of a β-bromine substituent may be calculated as 4.5/0.49 = 9.2.

II.6 Mechanistic Conclusions

The photobromination of cyclohexane and 1-

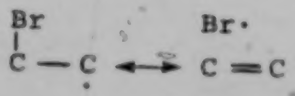
chlorobutane and their perdeuterated analogues is well described by a mechanism involving reversible hydrogen (or deuterium) atom abstraction. The reversal reaction is most important in the bromination of cyclohexane, as expected, since polar effects deactivate this reaction in the bromination of electronegatively substituted alkanes. This polar deactivation falls off as the distance of the radical centre involved from the substituent increases in the bromination of perdeuterio-1-chlorobutane.

The coincidence between the relative rates of bromination of cyclohexane and perdeuteriocyclohexane, and the relative rates of abstraction of the different hydrogens of 1-chlorobutane by bromine atoms, in the vapour phase reaction run with minimal interference from the reversal reaction, and the results obtained in liquid bromine solvent indicates that liquid bromine can scavenge all radicals, caged or "free", and that solution and vapour phase relative rates of the same kinetic order may be equated. Cage reversal between the geminate alkyl radicals-hydrogen (or deuterium) bromide pair is proposed to account for the differences between the vapour phase results and the solution phase results at lower bromine concentrations.

Solution phase bromination reactions are also complicated by reversal with the transfer species hydrogen tribromide. Transfer with this complex species is much faster than transfer with hydrogen bromide; consequently, reversible hydrogen abstraction is more important in solution than in the vapour phase.

The bromination of 1-bromobutane is complicated by elimination of bromine atoms from the β-bromobutyl radicals. In the vapour phase, the 1-butene thus formed is brominated in the allylic position primarily. In solution, however, all of the 1-butene formed adds bromine (ionically and/or free radically) to give 1,2-dibromobutane.

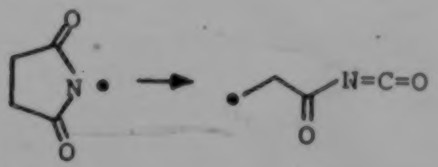
The rate of abstraction of the hydrogens (or deuteriums) β to the bromine substituent in 1-bromobutane and its perdeuterated analogue is accelerated by a factor of about 10 over what would be expected on the basis of polar effects only. If this acceleration is attributed to anchimeric assistance by the bromine substituent, it would lead to a bridged-bromine radical, and recent esr[124], CIDNP[125] and optical activity[64] results show that β-bromo-tert-butyl, β-bromoethyl and 3-bromo-2-butyl radicals are not bridged. The rate enhancement may be due to a hyperconjugative interaction between the bromine substituent and the radical centre, which stabilizes the β-bromobutyl radical, and therefore



$$\overset{Br}{C}-\dot{C} \longleftrightarrow \overset{Br\cdot}{C}=C \qquad (72)$$

weakens the bond strength of the C-H bonds, as has been previously suggested as an alternative explanation for the seemingly enhanced stability of β-bromoalkyl radicals.[78,126]

Whatever the origin of the effect, hydrogens β to the bromine substituent are abstracted more readily than any other hydrogens of 1-bromobutane. Since in NBS brominations of 1-bromobutane at low conversion of the NBS the major product is 1,3-dibromobutane,[78] it is likely that under these conditions the abstracting species are not bromine atoms but less selective radicals, probably succinimidyl radicals or carbon centered radicals derived from β-scission of succinimidyl radicals (equation 73). However, at higher conversions of NBS, the product distribution changes



(73)

to one very similar to that obtained in the bromination with molecular bromine,[78] and the relative rates of bromination of alkanes and substituted alkanes[44] are the same as with molecular bromine in the absence of reversal. It appears likely that at high conversion of NBS, the chain carriers are bromine atoms. The reason for the change in mechanism may be due to the build-up of a sufficient concentration of molecular bromine through adventitious coupling of bromine atoms to make this chain dominant. It is known that as the NBS brominations of alkanes and substituted alkanes proceed, the solutions quickly develop a bromine colour,[78,127] the intensity of which increases as the reaction proceeds.

It is possible that other NBS brominations, e.g. benzylic and allylic brominations, proceed through a nitrogen or carbon centered radical chain at the early stages of the reaction, while at higher conversion, the reaction goes through a bromine atom chain. Though in benzylic and allylic brominations there are no reports of the reactions developing a bromine colour, it is pertinent to note that the work done to establish the bromine atom chain in these brominations[16,39,115,128] involved relative rates, where the reactions were carried out to high (or complete) conversion of the NBS.*

II.7 General Method for Determining the Relative Rates of Transfer with Bromine and with Hydrogen Bromide in the Vapour Phase

The method presented in this thesis to determine the relative rates of transfer with bromine and with hydrogen bromide is not a general one, since it is restricted to perdeuterated substrates. Only a very small number of these is available commercially, and laboratory syntheses would generally be tedious. In this section, a general method for the determination of these relative rates using protiated compounds is presented. The method is best described by an example.

Suppose the relative rate of transfer of benzyl radicals with bromine and with hydrogen bromide is required. A vapour phase competitive bromination of toluene and cyclohexane is run under two conditions: (i) using a large excess of bromine; and (ii) using a large excess of bromine and of hydrogen bromide.

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* A cautionary note must be included. Since the completion of this work a large amount of 1,2,3,4-tetrabromobutane has been found as product in the bromination reactions of 1-bromobutane run at low concentrations of bromine. During the initial stages of the NBS reaction where the concentrations of molecular bromine are also, presumably, low, undetected tetrabromide could also be formed. The ultimate conversion of the β-radicals formed in these brominations into tetrabromide could account for the change in product ratios observed during the progress of the reaction, without having to invoke the presence of a new chain carrying species.

In the first case, reversal with hydrogen bromide will not be important if the reaction is run to low conversion of the bromine. Under these conditions, reactions 74-77 must be considered. The ratio

$$C_6H_{12} + Br \xrightarrow{k_1^c} C_6H_{11}^{\cdot} + HBr \qquad (74)$$

$$C_6H_{11}^{\cdot} + Br_2 \xrightarrow{k_2^c} C_6H_{11}Br + Br\cdot \qquad (75)$$

$$PhCH_3 + Br\cdot \xrightarrow{k_1^t} PhCH_2^{\cdot} + HBr \qquad (76)$$

$$PhCH_2^{\cdot} + Br_2 \xrightarrow{k_2^t} PhCH_2Br + Br\cdot \qquad (77)$$

of the rate of disappearance of toluene to that of cyclohexane is given by equation 78; this may be integrated

$$\frac{d[PhCH_3]/dt}{d[C_6H_{12}]/dt} = \frac{k_1^t[PhCH_3]}{k_1^c[C_6H_{12}]} \qquad (78)$$

and rearranged to give the relative rates of abstraction of hydrogen from toluene and from cyclohexane (equation 79).

$$\frac{k_1^t}{k_1^c} = \frac{\ln([PhCH_3]^f/[PhCH_3]^\circ)}{\ln([C_6H_{12}]^f/[C_6H_{12}]^\circ)} \qquad (79)$$

When the reaction is run in the presence of excess hydrogen bromide reactions 80-81 must also be

$$PhCH_2\cdot + HBr \xrightarrow{k_{-1}^{t}} PhCH_3 + Br\cdot \qquad (80)$$

$$C_6H_{11}\cdot + HBr \xrightarrow{k_{-1}^{c}} C_6H_{12} + Br\cdot \qquad (81)$$

considered. The relative rate of disappearance of substrates (or of appearance of products) is given by equation 82. Assuming a steady state concentration of

$$\frac{d[PhCH_3]/dt}{d[C_6H_{12}]/dt} = \frac{k_1^t[PhCH_3][Br\cdot] - k_{-1}^t[PhCH_2^{\cdot}][HBr]}{k_1^c[C_6H_{12}][Br\cdot] - k_{-1}^c[C_6H_{11}^{\cdot}][HBr]} \qquad (82)$$

benzyl and cyclohexyl radicals this equation may be rewritten to remove these radical concentrations (83).

$$\frac{d[PhCH_3]/dt}{d[C_6H_{12}]/dt} = \frac{k_1^t[PhCH_3]\left\{(k_{-1}^c/k_2^c)[HBr] + [Br_2]\right\}}{k_1^c[C_6H_{12}]\left\{(k_{-1}^t/k_2^t)[HBr] + [Br_2]\right\}} \qquad (83)$$

Under the conditions of the experiment, this expression may be integrated (equation 84). By using the previously

$$\frac{\ln([PhCH_3]^f/[PhCH_3]^\circ)}{\ln([C_6H_{12}]^f/[C_6H_{12}]^\circ)} = \frac{k_1^t}{k_1^c}\left(\frac{(k_{-1}^c/k_2^c)[HBr] + [Br_2]}{(k_{-1}^t/k_2^t)[HBr] + [Br_2]}\right) \qquad (84)$$

determined value of (k_1^t/k_1^c), and the value of k_2^c/k_{-1}^c for perdeuteriocyclohexane reported in this work (Table 5), equation 84 may be used to give the value of k_2^t/k_{-1}^t for toluene.

Thus by comparing the relative rates of bromination of two substrates with excess bromine with and without excess hydrogen bromide in the gas phase, the relative rate of transfer with bromine and with hydrogen bromide may be determined.

EXPERIMENTAL

III.1 Materials

1-Bromobutane and 1-chlorobutane were commercially available chemicals. They were purified by washing with concentrated sulphuric acid and with water, drying over anhydrous sodium sulphate, and fractionally distilled. Glpc showed them to be >99.9% pure. Cyclohexane and toluene (Phillips 66, research grade, >99.9%) were used without further purification.

All perdeuterated compounds were obtained from Merck, Sharp & Dohme Co. of Canada Limited. Perdeuteriocyclohexane and perdeuterio-1-bromobutane were purified by two preparative glpc collections (6 m x 5 mm 10% Carbowax 20 M on Chromosorb P AW, glass column, 50°); perdeuterio-1-chlorobutane was used as supplied. Glpc analysis of the deuterated compounds prior to use showed them to be more than 99.5% pure. Mass spectral analysis (AEI MS9, 12 ev) showed them to contain 99.4 (C_6D_{12}), 98.4 (C_4D[illegible]Cl) and 98.3 (C_4D_9Br) atom % deuterium. H^1 100 MHz nuclear magnetic resonance spectroscopy (Varian HA100) showed a single signal for perdeuteriocyclohexane (τ, 8.59), and four singlets for perdeuterio-1-chlorobutane (τ, 9.12, 8.59, 8.32, 6.58, see Figs. 3 and 4) and for perdeuterio-1-bromobutane (τ, 9.11, 8.60, 8.24, 6.67, see Figs. 7 and 8) due to the residual protium in the compounds.

Bromocyclohexane, trans-1,2-dibromocyclohexane, 1,2-dibromobutane, 1,3-dibromobutane, 1,4-dibromobutane, 4-bromo-1-chlorobutane, chlorobenzene and o-dichlorobenzene were commercially available chemicals, and were purified by preparative glpc collection. 1,1-Dibromobutane was prepared by Dr. Y. Kosugi in these laboratories by the Hunsdicker reaction on 2-bromopentanoic acid. It gave small parent peaks at m/e 214, 216, 218 (ratio 1:2:1), and its nmr spectrum was consistent with its structure: CCl_4, TMS internal standard, τ 9.01 (t, J = 6.9 Hz, 3H), τ 8.40 (sextet, J = 6.9 Hz, 2H), τ 7.61 (q, J = 7 Hz, 2H) and τ 4.28 (t, J = 6.9 Hz, 1H). 1,2,2-Tribromobutane and 1,3,3-tribromobutane were prepared by Dr R. J. Arhart (see Appendix 4).

A mixture of 1-bromo-, 2-bromo- and 3-bromo-1-chlorobutane was obtained from the preparative glpc collection (3 m x 5 mm 10% UCON 50 LB550X on Chromosorb P AW, glass column, 110°) of the products of the liquid phase photobromination of 1-chlorobutane with molecular bromine.[66] They were identified by comparison of their glpc retention times with those of the authentic materials prepared by Dr. J. E. Rowe.[129]

A mixture of 2,3-dibromo-1-chlorobutane and 1,2-dibromo-3-chlorobutane was prepared by the addition of a carbon tetrachloride solution of bromine to commercial crotyl chloride (Aldrich technical grade, containing 20% 3-chloro-1-butene; glpc showed the presence of these two compounds in a ratio of 3:1) in carbon tetrachloride at 0°. The crude product was purified by distillation, bp 78-79° (8.7 mm), $\underline{n}_D^{25}$ 1.5385. The nmr spectrum (CCl_4) showed two doublets (τ, 8.13, J = 6.3 Hz; τ, 8.19, J = 6.6 Hz; 3H) in the ratio of 2.7:1 and two sets of multiplets centered at τ, 6.02 (2H) and τ, 5.59 (2H). The mixture did not give a parent peak in the mass spectrum (70 ev), but gave peaks at m/e 173, 171 (base peak), 169 (P-Br, ratio 3:4:1), 217, 215, 213 (P-Cl, very small), 135, 133 (ratio 1:1) and 91, 89 (ratio 3:1). The two compounds were not separated by glpc (3 m x 5 mm 10% UCON 50 LB550X), but the glpc showed the mixture to be >99.9% pure.

Anal. Calc. for $C_4H_7Br_2Cl$: C, 19.20; H, 2.82. Found, C, 18.93; H, 2.85.

1,2,3-Tribromobutane was prepared in a similar way by addition of bromine to commercial crotyl bromide. The reaction mixture was washed with 10% aqueous sodium bisulphite and with water, dried (Na_2SO_4) and distilled. It was obtained as a colourless liquid, bp 110° (16.6 mm), $\underline{n}_D^{20}$ 1.5684 (lit.[130] bp 97° (10 mm), $\underline{n}_D^{20}$ 1.5680). The nmr spectrum showed the methyl protons as two doublets (τ, 8.15, J = 6.3 Hz; τ, 8.20; J = 6.7 Hz; 3H) and the other protons as a complex pattern at τ, 6.4-5.2 (4H).

1-Butene (Phillips research grade, 99.9%) was degassed in a vacuum line and distilled prior to use. 1-Bromo-2-butene and 3-bromo-1-butene were obtained by preparative glpc collection (6 m x 5 mm 10% Carbowax) from commercial technical grade crotyl bromide. Both compounds gave parent peaks in the mass spectrum at m/e 134, 136 (ratio 1:1); the nmr spectrum of 1-bromo-2-butene (CCl_4, TMS internal standard) was consistent with its structure; it showed an apparent doublet at τ 8.26 (J = 6.5 Hz, 3H), and two multiplets at τ 5.85-6.2 and τ 3.8-4.7, each integrating for two hydrogens. The nmr spectrum of 3-bromo-1-butene was more complex; it showed a doublet at τ 8.23 (J = 6.4 Hz, 3H), and a multiplet at τ 3.5-5.7 integrating for four hydrogens.

1,1-Diphenylethene (Aldrich) was distilled prior to use, bp 136.5-137.0° (9 mm), $\underline{n}_D^{20}$ 1.6088 (lit.[131] bp 139 (11 mm), $\underline{n}_D^{20}$ 1.6085); nmr spectroscopy and glpc analysis showed it to have no detectable impurities.

Freon 113 (Matheson) and Freon 112 (PCR) were distilled from phosphorus pentoxide through a 30 cm Vigreux column, bp 45.5° and 88.0° (700 mm) respectively. For the equilibrium constant measurements, Freon 113 was washed with water (1x), 1 M hydrochloric acid (2x) 1 M sodium hydroxide solution (3x) and water (3x), refluxed over anhydrous calcium chloride overnight, distilled through a 60 cm teflon spinning band column, and finally distilled from phosphorus pentoxide, the middle cut being collected.

Molecular bromine (McArthur Chemical Co., reagent grade) was washed with concentrated sulphuric acid and freshly distilled from phosphorus pentoxide, bp 57.3° (700 mm). Bromine-81 was obtained from Isotope Development Centre, Oak Ridge National Laboratory;

it was distilled by trap to trap distillation prior to use.

Hydrogen bromide (Matheson) was introduced into a vacuum system through molecular sieves 4A or anhydrous calcium chloride, frozen in liquid nitrogen, and the noncondensible gases pumped off until the pressure was less than 0.1μ. The solid hydrogen bromide was sublimed twice at -98° (methanol slush bath) and finally distilled.

III.2 Gas Liquid Partition Chromatography (glpc)

For glpc analyses, four instruments were used: a Carlo Erba Fractovap Model GV, a Varian Aerograph Model 1520 and Model 90P, and a Hewlett Packard HP 401 chromatograph. The first three instruments were equipped with a thermal conductivity detector; the HP 401 had a flame ionization detector. Glass columns were used throughout; the columns are specified in the individual experiments. All compounds studied were stable on the column used.

Analyses were carried out at least in triplicate. Peak areas were calculated by disc or electronic integrators, or by multiplying the peak height by the width at half height.[132] Calibration curves were constructed to convert the area ratios of the compounds relative to the internal standard into mol ratio.[132] When quoted, the experimental uncertainties are average deviations from the mean value obtained from different reactions. Retention time comparison and peak enhancement (spiking) refer to the addition of authentic material to a portion of the sample and reanalysis by glpc.

III.3 Physical Constants

All boiling points reported are uncorrected. Refractive indices were measured on a Bausch and Lomb refractometer.

III.4 General Procedure for the Determination of the Relative Rates of the Perdeuterated Substrates in the Vapour Phase

About 0.5 g perdeuterated compound (RD) was carefully weighed into a Pyrex breakseal, and this was degassed by the freeze-thaw method three times and finally sealed. Bromine was similarly weighed, degassed and sealed in a separate breakseal. Hydrogen bromide was measured by pressure in a known volume at a known temperature on a vacuum line, distilled into a breakseal, and the breakseal was sealed. The three breakseals were attached to the reaction bulb (5, 12 or 22 l), and the system was evacuated to less than 0.1μ. The bulb was isolated from the vacuum line by means of a teflon "Rotaflo" stopcock, and the breakseals were broken in the absence of light (in the order RD, hydrogen bromide, and bromine, with twenty minute intervals between each breakseal). The mixture of the three reactants was allowed to equilibrate for about thirty minutes, and then the bulb was photolyzed (one 100 W incandescent lamp). The contents of the bulb were condensed in the absence of light into a tube attached to the bulb. The tube was opened, an internal standard added (o-dichlorobenzene for perdeuteriocyclohexane and for perdeuterio-1-chlorobutane, and chlorobenzene for perdeuterio-1-bromobutane), and the excess bromine and hydrogen bromide were destroyed with cold (0°) aqueous sodium bisulphite (10%). The organic substrates were extracted with Freon 113 (about 25 ml), the Freon solution washed with cold water and dried ($MgSO_4$). It was analyzed by glpc (2 m x 5 mm 10% UCON 50 LB550X on Chromosorp P AW, glass column) for starting material and products. The solution was concentrated on a 60 cm teflon spinning band column to about 4 ml, and the unreacted starting material collected and recollected by preparative glpc (6 m x 5 mm 10% Carbowax 20 M, 50°).

The control experiments that were performed to check the recovery and isolation of the starting material and products were done as described above, except that a breakseal containing the products was also attached to the reaction vessel. The products were introduced into the reaction bulb with the other three substrates, and the mixture was allowed to stand in the absence of light for at least one hour. The contents were then collected and isolated and analyzed as above. The results are given in Table 29.

III.4.1 Determination of Residual Protium in the Perdeuterated Substrates

i. Using Mass Spectrometry

The perdeuterated substrate was analyzed on an AEI MS9 spectrometer at about 12 ev, using slow magnetic scanning to eliminate peak clipping by the galvanometers. Two samples of RD were scanned five times on the molecular ion region, and from the average

Table 29

Control Reactions on the Recovery and Isolation Procedures[a]

Compound	Initial Mol[b]	Recovered Mol[b]	%[c]
	A. For Cyclohexane Brominations		
Cyclohexane	611.6	602.4	98.5
Bromocyclohexane	65.62	64.81	98.8
Trans-1,2-dibromocyclohexane	3.835	3.883	101.3
Bromine	784.4	-	-
Hydrogen Bromide	3903	-	-
	B. For 1-Chlorobutane Brominations		
1-Chlorobutane	553.0	513.7	92.9
1-Bromo-1-chlorobutane	8.425	8.224	97.7
2-Bromo-1-chlorobutane	10.05	9.739	96.9
3-Bromo-1-chlorobutane	17.48	17.03	97.4
4-Bromo-1-chlorobutane	4.422	4.211	95.5
Trihalide[d]	7.550	7.719	102.2
Bromine	946.6	-	-
Hydrogen Bromide	7484	-	-
	C. For 1-Bromobutane Brominations		
1-Bromobutane	328.4	301.8	91.9
1,2-Dibromobutane	41.26	40.52	98.2
1,3-Dibromobutane	5.928	5.779	97.5
1,4-Dibromobutane	7.180	7.110	99.0

continued.....

Table 29 (cont'd.)

Compound	Initial Mol[b]	Recoverd Mol[b]	%[c]
1,2,3-Tribromobutane	6.071	5.899	97.2
Bromine	2011	-	-
Hydrogen Bromide	16290	-	-

[a] All controls were run using a 22 l reaction vessel.

[b] Number of mols used at start and observed by glpc at end of run, x 10^5.

[c] Percent recovered to initial mols.

[d] Mixture of 1,2-dibromo-3-chlorobutane and 2,3-dibromo-1-chlorobutane.

heights of the peaks, the fraction of protium in the sample was determined by the method of Biemann.[133] This gave the total amount of protium in RD. For perdeuterio-1-chlorobutane the amount of protium at each position of the molecule was then determined from the ratio of the signals of the different protons in the 100 MHz H^1 spectrum.

In a typical run, the peak heights of the recovered perdeuteriocyclohexane from reaction 2 (Table 5) are given in Table 30. All the peaks were sharp and unsplit. The peak heights were corrected for the C^{13} contribution; this was calculated initially from the ratio of the 97/96 peaks. An iterative treatment was used until a constant value of the C^{13} correction and of the peak heights was obtained; these values are given in Table 30. The percentage protium in the sample was then calculated from equation 85,

$$RH = \frac{95 + 2(94) + 3(93)}{96 + 95 + 94 + 93} \times 100 \qquad (85)$$

where 95 is the height of the mass spectral peak at m/e 95, etc. The amount of protiated perdeuterio-cyclohexane was then calculated as shown in footnote b of Table 14.

Table 30

Determination of Protium Content of Perdeuteriocyclohexane by Mass Spectroscopy[a]

m/e	Peak Assignment	Peak Height, mm[b]	Corrected Peak Height[c]
97	$C_5C^{13}D_{12}$	6.8 ± 0.1	6.8
96	C_6D_{12}, $C_5C^{13}D_{11}H$	100.0 ± 0.1	98.3
95	$C_6D_{11}H$, $C_5C^{13}D_{10}H_2$	25.5 ± 0.1	25.2
94	$C_6D_{10}H_2$, $C_5C^{13}D_9H_3$	4.2 ± 0.2	4.2
93	$C_6D_9H_3$	0.5 ± 0.0	0.5
92	$C_6D_8H_4$	not observed	-

[a] Perdeuteriocyclohexane recovered from reaction 2, Table 5 analyzed on an AEI MS9 at 10 ev.

[b] Average value of two samples, each sample being scanned five times, relative to peak at m/e 96, arbitrarily set as 100.

[c] Corrected for the C^{13} contributions in peaks at m/e 96, 95, and 94; the correction was initially set as 6.8%, the 97/96 ratio.

The total amount of protium incorporated into perdeuterio-1-chlorobutane was determined as follows. If A_o is the percentage of $C_4D_9Cl^{35}$, B_o the percentage of $C_4D_8HCl^{35}$ and C_o the percentage of $C_4D_7H_2Cl^{35}$ in the sample before reaction, and if the fractional amount of incorporation of protium during the reaction is X, then the amounts of these three species after reaction, A, B and C, may be calculated as shown below. It was

$$\begin{tikzcd}
 & \text{Before Reaction} & \text{After Reaction} \\
d_9 & A_o \arrow[r, "(1-X)"] \arrow[dr, "X"'] & A_o(1 - X) = A \\
d_8 & B_o \arrow[r, "(1-X)"] \arrow[dr, "X"'] & A_oX + B_o(1 - X) = B \\
d_7 & C_o = 0 & B_oX = C
\end{tikzcd}$$

assumed that the amount of C_o, the d_7 species, was negligible before reaction. This is not unreasonable, since the sample contained less than 2 atom % H^1. From this analysis, the ratio of d_8/d_9 after reaction, B/A, may be expressed as in equation 86. If the values of A_o, B_o, A and B are known, this equation may be used

$$\frac{B}{A} = \frac{A_oX + B_o(1 - X)}{A_o(1 - X)} \qquad (86)$$

to solve for X, the fractional amount of protium that was incorporated during the reaction. The values of A_o,

B_o, A and B were determined by a method developed by Dr. H. Takiguchi of this laboratory (see Appendix 5). The calculated fractional incorporation by mass spectroscopy using this method always was in very good agreement with that calculated by nmr (see below).

ii. Using Nuclear Magnetic Resonance Spectroscopy

Accurately prepared solutions of RD and 1,1-diphenylethene in Freon 113 were analyzed by nmr spectroscopy using a Varian HR 100 spectrometer. Two spectra were run (normal and deuterium decoupled) with the phenyl protons as lock and reference. A small amount of TMS was added, and two more spectra, normal and deuterium decoupled, were run, with TMS as lock and reference (see Figs. 3, 4, 7, 8). Each spectrum was integrated at least five times, and the average values for the integrated areas were again averaged for the four spectra. Both decoupled and undecoupled spectra gave the same integration values, within experimental error, showing the absence of any experimentally important Overhauser effects. From the relative areas of the signal/s from RD and the olefinic protons of 1, 1-diphenylethene (τ, 4.63), the amount of protium in each position of RD could be determined.

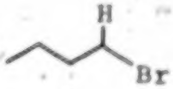
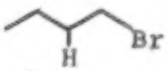
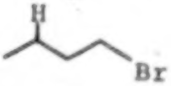
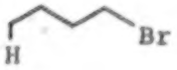
In a typical run, a solution containing 1.075 x 10^{-3} moles perdeuterio-1-bromobutane recovered from reaction 4 (Table 25) and 1.709 x 10^{-5} moles 1,1-diphenylethene was analyzed by nmr (Table 31). The concentration of R^iH for each position was determined as shown in footnote c of Table 14.

III.5 Determination of the Equilibrium Constant

Solutions of bromine in Freon 113 (1% in TMS) were prepared and aliquots were titrated iodometrically with thiosulphate. One milliliter aliquots were quantitatively transferred into 4 mm I.D. nmr tubes which were fitted with a ground glass joint. The tubes were attached to a vacuum line, frozen in liquid nitrogen and degassed to less than 2μ. A premeasured amount of hydrogen bromide was distilled into the tubes and the tubes were sealed. The tubes were shaken and allowed to equilibrate at probe temperature, 32.8 ± 0.2° or 23.0 ± 0.2°, and the nmr spectrum obtained. Only one signal was observed in the spectra. All line positions were measured in Hertz relative to TMS by counting the difference between the lock and sweep occillator frequencies using a Varian HA 100 spectrometer. Reproducibility of the measurement was better than

Table 31

Determination of Protium Content in Each Position of Perdeuterio-1-Bromobutane by NMR Spectroscopy[a]

Proton	Area[b]	Moles[c] $\times 10^5$	% Protium[d]	$[R^iH]$[e]
$\phi_2C{=}CH_2$	1.000	3.417	-	-
	2.027±0.044	6.926	6.44	1.03
	1.477±0.016	5.047	4.69	0.66
	1.539±0.055	5.259	4.89	0.70
	2.534±0.109	8.659	8.05	1.26

[a] Perdeuterio-1-bromobutane (0.15752 g, 1.0751×10^{-3} mol) recovered from reaction 4, Table 25, and 1,1-diphenylethene (0.00308 g, 1.7087×10^{-5} mol) in 0.3 ml Freon 113 analyzed on a Varian HA-100 spectrometer at ambient temperature.

[b] Average of twenty integrations from four spectra (see text), relative to the olefinic protons of 1,1-diphenylethene.

[c] Obtained by multiplying the area relative to the olefinic protons by 3.417×10^{-5}.

[d] Defined as moles H^1 in a position relative to the total

continued.....

Table 31 (cont'd.)

number of moles of perdeuterio-1-bromobutane, expressed as percentage.

[e] Concentration (M x 10^5) of perdeuterio-1-bromobutane protiated at position i; calculated from the equation in footnote b, Table 14.

0.2 Hz. To check the bromine solvent shift, 2,2-dimethylpropane (Phillips 66, research grade, 99.9%) was substituted for the hydrogen bromide, and the tubes were protected from light by wrapping with aluminum foil.

The results are given in Tables 7, 8, 9 and 10. The value of the equilibrium constant was determined as described in the text (section II.2.4).

III.6 Relative Rates of Bromination of Cyclohexane and Perdeuteriocyclohexane in the Vapour Phase

Aliquots (0.20 ml) of a solution of cyclohexane (1.312 M), perdeuteriocyclohexane (1.275 M), Freon 112 (1.402 M, internal standard) and bromine (10.26 M) were placed in Pyrex breakseals, and these were degassed once by the freeze-thaw method and sealed. The breakseals were attached to a 5 l reaction bulb; in reactions 4 and 5 (Table 11) a second breakseal containing a known amount of bromine was also attached to the reaction vessel. The bulb was degassed to less than 0.1μ, isolated from the vacuum line by a teflon "Rotaflo" stopcock, and the substrates introduced into the vessel in the dark. They were allowed to equilibrate for thirty minutes, when the bulb was irradiated (one 100 W incandescent lamp) for sufficient time to ensure at least 12% reaction of cyclohexane-d_{12}. The contents of the bulb were condensed, and the excess bromine destroyed with ice-cold 10% aqueous sodium bisulphite. One milliliter Freon 113 was added, and the Freon solution washed once with water and dried ($MgSO_4$). The reaction mixture was then analyzed by glpc on a 7.5 m x 6 mm glass column packed with 7.5% UCON 50 LB 550X on Chromosorp P AW, 80-100 mesh. Controls on the recovery from the reaction bulb and on the work-up showed that >98% of the substrates and internal standard could be recovered, and that the ratios C_6D_{12}/Freon 112, C_6H_{12}/Freon 112 and C_6H_{12}/C_6D_{12} did not change within experimental error (± 1.8%). The results are given in Table 11.

The unbrominated cyclohexane and perdeuteriocyclohexane were collected together by preparative glpc (3 m x 5 mm 10% UCON 50 LB 550X, 50°). The mixture was analyzed by mass spectrometry (AEI MS9, 12 ev), and the amount of protium in perdeuteriocyclohexane and the amount of deuterium in cyclohexane was calculated by the method of Biemann.[133] The results are given in Table 12.

III.7 Photobrominations of 1-Chlorobutane with Molecular Bromine

Aliquots (0.500 ml) of a solution of 1-chlorobutane (7.447 g, 8.045 x 10^{-2} mol) and bromine (1.315 g, 8.226 x 10^{-3} mol) were transferred into each of twelve breakseals. Each breakseal was in turn attached to a 5 l reaction vessel and this was degassed. The vessel was isolated by a teflon "Rotaflo" stopcock from the vacuum line, and the contents of the breakseal introduced into it. After equilibration in the absence of light (30 minutes), the reaction bulb was irradiated (one 100 W incandescent lamp) for the appropriate time, and then the contents were condensed into a tube attached to the bulb. To the isolated mixture was added 20 ml 5% aqueous potassium iodide solution and an aliquot of a Freon 113 solution containing a known amount of o-dichlorobenzene (internal standard). The mixture was titrated iodometrically for bromine and for hydrogen bromide.[134] The organic layer was separated, washed once with water, dried ($MgSO_4$) and analyzed by glpc (2 m x 5 mm 10% UCON 50 LB 550X). Only 1-bromo-, 2-bromo-, and 3-bromo-1-chlorobutane were detected; the material balance (based on bromine) was always greater than 98.7%. The results are listed in Table 16.

For the computation of the ratios $f^{\alpha/\gamma}$ and $f^{\beta/\gamma}$, the experimental values obtained at time t for the concentrations of each of the three brominated chlorides were plotted as a function of the ratio $[Br_2]/[HBr]$ ($\bar{x}$) at time t. The experimental curves were fitted by a least squares program to the exponetial function given in expression 56; the data was divided into two sections and the curves fitted in parts. The first five points had a standard deviation of less than 3×10^{-3} mol/l; the last five points had a standard deviation less than 6×10^{-3} mol/l. The slopes of the experimental curves, obtained by differentiation of the appropriate equation 56, were also obtained from the manually plotted curves. The agreement between the slopes obtained by the two methods were within the expected range that would be due to experimental error in the determination of the concentration of the bromochlorobutanes.

The solution phase reactions of Table 18 were run in Freon 113. An aliquot of Freon 113 solutions of 1-chlorobutane, bromine and Freon 112 (internal standard) were placed in Pyrex tubes which had a ground glass joint attached. The tubes were degassed three times by the freeze-thaw method and sealed. The vapour space above the solution was less than 0.3 ml. The tubes were placed in a water bath thermostatted at 21°, equilibrated for ten minutes in the absence of light, and then photolyzed (one 100 W incandescent lamp) till about 1-10% of the 1-chlorobutane had brominated. The tubes were opened, the excess bromine destroyed in the usual manner, and the solutions analyzed by glpc (3 m x 5 mm 10% UCON 50 LB 550X). No dibrominated chlorobutanes were detected; the relative amounts of 1-bromo-1-chlorobutane and 2-bromo-1-chlorobutane to 3-bromo-1-chlorobutane observed are given in Table 18.

A control experiment was performed to check the stability of the products in 12 M bromine solution. A solution containing 1-bromo-1-chlorobutane (1.07×10^{-3} M), 2-bromo-1-chlorobutane (1.26×10^{-3} M), 3-bromo-1-chlorobutane (2.20×10^{-3} M), 4-bromo-1-chlorobutane (5.54×10^{-4} M), bromine (12 M) and Freon 112 (internal standard, 1.63×10^{-2} M) in Freon 113 was left in the absence of light under the same conditions as the photoinitiated reactions. Aliquots were periodically withdrawn, the bromine destroyed with ice-cold aqueous sodium bisulphite solution (10%), the organic solution dried ($MgSO_4$) and analyzed by glpc. The ratio of the brominated chlorides to Freon 112 was found to remain unchanged over the same period of time as the photoinitiated reactions were run, showing that the products were stable under these conditions.

III.8 Vapour Phase Bromination of 1-Bromobutane with Bromine-81

Two breakseals containing 1-bromobutane (2.25×10^{-3} mol) and bromine (96.04% Br-81, 3.96% Br-79, 3.75×10^{-4} mol) respectively were attached to a 5 l reaction vessel and this was degassed to <1μ. The two reactants were introduced into the reaction bulb, allowed to equilibrate in the absence of light for 15 min., and then the bulb was irradiated till all the bromine colour was discharged. The contents of the bulb were collected and the unreacted 1-bromobutane, 1,2-dibromobutane, 1,3-dibromobutane and 1,2,3-tribromobutane were collected by preparative glpc (2 m x 5 mm 10% DEGS on Diatoport, glass column), and analyzed by mass spectrometry on an AEI MS9 spectrometer at 15 and 70 ev. The relative intensities of the parent peaks were independent of the ionization voltage within experimental error. The results are given in Table 21.

III.9 Photobromination of 1-Bromobutane in the Vapour Phase under "Normal" Bromination Conditions

Into a 5 l bulb that had been evacuated to less than 1μ, were distilled approximately 1.3×10^{-3} mol 1-bromobutane and 2.5×10^{-4} mol bromine. The bulb was degassed again and sealed. The substrates were allowed to vapourize and equilibrate in the dark for thirty minutes, and then the bulb was irradiated with a 40 W incandescent lamp. After the photolysis, the contents were condensed, and the condensed mixture was added to 70 ml water containing 2 g potassium iodide, and the solution titrated iodometrically for bromine and hydrogen bromide. One milliliter of chlorobenzene solution (internal standard) was added, and the organic solution washed with water and dried ($MgSO_4$). It was then analyzed by glpc (4 m x 5 mm 15% DIDP on Chromosorp W AW, glass column). The results are shown in Table 22; products were identified by peak enhancement with authentic materials.

III.10 Photobromination of 1-Bromobutane with Excess Bromine

These reactions were run as described in the general procedure for the perdeuterated substrates. The amounts of substrates used and products observed (using 3 m x 5 mm 5% Carbowax 20 M on Chromosorp P AW, glass column, and 2 m x 5 mm 10% DEGS on Diatoport S, glass column) are given in Tables 23 and 27. The material balance (on 1-bromobutane) was always greater than 96%.

III.11 Liquid Phase Bromination Using Gas Phase Concentrations

Three litres Freon 113 were placed in a three-necked flask equipped with a gas bubbler, thermometer and double surface condenser, the outlet of which was protected by a calcium chloride drying tube. The flask was placed in a water bath, and the Freon was flushed with dry argon for 70 minutes, during which time it was also stirred magnetically. In subdued light, 4 ml of a Freon 113 solution of 1-bromobutane (0.209 M) and 2 ml of a Freon 113 solution of bromine (0.0988 M) were added. The solution was stirred in the dark for 10 minutes, and then it was irradiated (two 200 W incandescent lamps) for 5 hours. The temperature during the photolysis was 25-28°. One milliliter of a Freon 113 solution of chlorobenzene and o-dichlorobenzene (internal standards) was added, and the solution was washed with 100 ml aqueous sodium bisulphite (8%) and with water (150 ml). It was dried ($MgSO_4$) and then carefully concentrated by distillation of the Freon on a 60 cm teflon spinning band column to about 7 ml. The concentrated solution was analyzed by glpc (2 m x 5 mm 10% DEGS on Diatoport S). The results are given in Table 23; the ratio of chlorobenzene to o-dichlorobenzene was the same, within experimental error, after the distillation as in the original solution. The products were identified by spiking with authentic materials. The material balance based on bromine was 97.7%

III.12 Vapour Phase Bromination of 1-Butene

1-Butene was measured in a vacuum line, and distilled into a breakseal sealed. Bromine was weighed in a small tube, the tube dropped into a breakseal, and this was degassed once and sealed. The breakseals were attached to the reaction vessel (5, 12 or 22 l), and after this was evacuated to less than 0.3μ the bromine was introduced into the bulb and allowed to equilibrate for at least ten minutes. The 1-butene breakseal was then broken: in the reactions were the reactants were not allowed to equilibrate, the irradiation of the bulb was started before the butene breakseal was broken. The bromine colour was discharged instantaneously (<5 sec.). The contents of the bulb were collected, an internal standard (chlorobenzene) and some solid sodium bicarbonate added, and the solution analyzed by glpc (3 m x 3 mm 5% Carbowax 20 M on Chromosorp P AW, glass column). Four products were detected, other than unreacted 1-butene; these were identified by spiking with authentic materials as 1-bromobutane, 3-bromo-1-butene, 1-bromo-2-butene and 1,2-dibromobutane. The reaction mixture was also analyzed on a 3 m x 5 mm 20% Silicon Oil 200 on Chromosorp W at 23° to check if any 2-butene was formed. The products were collected by preparative glpc (3 m x 5 mm 10% Carbowax 20 M TPA on Chromosorp P AW, glass column). 1-Bromobutane was collected as a mixture with 3-bromo-1-butene. The nmr and mass spectra of these products were identical with those of the authentic materials. A control mixture of 1-bromobutane and 3-bromo-1-butene showed that 1-bromobutane could easily be detected by nmr and mass spectroscopy.

III.13 Competitive Bromination of the Allylic Bromides and 1-Bromobutane in the Vapour Phase

An aliquot (0.2 ml) of a Freon 113 solution of

1-bromobutane (1.542 M) and a mixture of 1-bromo-2-butene and 3-bromo-1-butene (1.691 M) was placed in a breakseal, which was then degassed and sealed. Into a second breakseal was weighed 0.0456 g (2.85×10^{-4} mol) bromine, and it was degassed and sealed. The breakseals were attached to a 5 l reaction bulb and this was degassed. After the allylic bromides and 1-bromobutane had been allowed to equilibrate in the bulb, the bromine breakseal was broken and the bulb was irradiated at the same time (one 60 W incandescent lamp). The bromine colour was discharged in less than 5 sec. After the contents of the bulb were collected, an aliquot of a chlorobenzene solution in Freon 113 (internal standard) and some solid sodium bicarbonate were added, and the solution analyzed for starting materials (6 m x 3 m 5% UCON POLAR on Chromosorp W) and for products (6 m x 3 mm 5% DEGS on Chromosorp W). Glpc showed that the solution contained $3.040 \pm 0.050 \times 10^{-4}$ mol 1-bromobutane, $5.186 \pm 0.078 \times 10^{-5}$ mol allylic bromides, $3.05 \pm 0.01 \times 10^{-6}$ mol 1,2-dibromobutane, $1.48 \pm 0.01 \times 10^{-6}$ mol 1,3-dibromobutane and $2.737 \pm 0.003 \times 10^{-4}$ mol 1,2,3-tribromobutane. The products were identified by comparison of their retention times with that of authentic materials, and by spiking.

Since both 1-bromobutane and the allylic bromides can give 1,2,3-tribromobutane on bromination, the amount of this product formed from 1-bromobutane was calculated as follows. The initial ratio of 1-bromobutane (RBr) to allylic bromides (ABr) was 1.0966. If the amount of tribromide formed from 1-bromobutane was x, the initial ratio of RBr:ABr may be expressed as in equation 87, where it is assumed that the dibromides arise from

$$\frac{(\mathrm{RBr})^{\circ}}{(\mathrm{ABr})^{\circ}} = \frac{(\mathrm{RBr})^{f} + (1,2) + (1,3) + (x)}{(\mathrm{ABr})^{f} + (1,2,3) - (x)} \qquad (87)$$

bromination of 1-bromobutane. The value of x was found to be 6.13×10^{-6} mol; the rate of bromination of the allylic bromides (k_a) relative to that of 1-bromobutane (k_b) was then calculated as in equation 88.

$$\frac{k_a}{k_b} = \ln\left(\frac{(\mathrm{RBr})^{f}+(1,2)+(1,3)+(x)}{(\mathrm{RBr})^{\circ}}\right)\bigg/\ln\left(\frac{(\mathrm{ABr})^{f}+(1,2,3)-(x)}{(\mathrm{ABr})^{\circ}}\right) \qquad (88)$$

III.14 Photobromination of 1-Butene with Excess Bromine

Three breakseals, containing 1-butene (7.927×10^{-5} mol), bromine (1.891×10^{-3} mol) and toluene (Phillips research grade, 1.16×10^{-2} mol) respectively, were attached to a 22 l reaction bulb, which was degassed and isolated from the vacuum line. The bromine was introduced into the bulb and allowed to equilibrate for 15 min.;

the bulb was irradiated (one 100 W incandescent lamp) and the alkene was introduced into the reaction vessel. After 5 sec., the toluene breakseal was broken and the system irradiated for a further 30 min. The contents of the bulb were collected, an aliquot of a Freon 113 solution of chlorobenzene and some solid sodium bicarbonate added, and the solution was analyzed by glpc (2 m x 5 mm 10% UCON 50 LB 550X). Only three products were detected, 1,2-dibromobutane (6.5×10^{-6} mol), benzyl bromide (1.812×10^{-3} mol) and 1,2,3-tribromobutane (6.62×10^{-5} mol). The material balance on bromine was 99.7%.

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APPENDIX 1

The Cage Effect in the Photobromination of Perdeuterio-1-Halobutanes with Excess Bromine and Excess Hydrogen Bromide

The solution phase bromination of alkanes and substituted alkanes differs from the vapour phase reaction (Scheme 1) in that cage filtering is present and reversal with hydrogen tribromide is important. The proposed mechanism for the bromination of perdeuterio-1-chlorobutane in solution is given in Scheme 4. The rate of formation of perdeuterio-1-bromo-1-chlorobutane ($R^{\alpha}Br$) is given by equation 89, while that of perdeuterio-1-protio-1-chlorobutane ($R^{\alpha}H$) is given by equation 90. The ratio of the rates of formation of $R^{\alpha}Br$ and $R^{\alpha}H$ is given by expression 91, which under the reaction

$$d[R^{\alpha}Br]/dt = k_2[R\cdot][Br_2] \tag{89}$$

$$d[R^{\alpha}H]/dt = k_{-1}[R\cdot][HBr] + k'_{-1}[R\cdot][HBr_3] \tag{90}$$

$$\frac{d[R^{\alpha}H]/dt}{d[R^{\alpha}Br]/dt} = \frac{k_{-1}[HBr] + k'_{-1}[HBr_3]}{k_2[Br_2]} \tag{91}$$

conditions, i.e. when the concentrations of bromine and hydrogen bromide (and consequently hydrogen tribromide) do not change significantly, may be integrated (equation 92). Adding 1 to each side of this expression and rearrangement gives equation 93.

$$\frac{[R^{\alpha}H]^{f}-[R^{\alpha}H]^{\circ}}{[R^{\alpha}Br]} = \frac{k_{-1}[HBr]+k'_{-1}[HBr_3]}{k_2[Br_2]} \tag{92}$$

$$\frac{[R^{\alpha}H]^{f}-[R^{\alpha}H]^{\circ}+[R^{\alpha}Br]}{[R^{\alpha}Br]} = \frac{k_{-1}[HBr]+k'_{-1}[HBr_3]+k_2[Br_2]}{k_2[Br_2]} \tag{93}$$

The ratio of the rates of formation of perdeuterio-1-bromo-1-chlorobutane and perdeuterio-3-bromo-1-chlorobutane ($R^{\gamma}Br$) is given by equation 94.

$$\frac{d[R^{\alpha}Br]/dt}{d[R^{\gamma}Br]/dt} = \frac{k_2[R\cdot^{\alpha}]}{k_6[R\cdot^{\gamma}]} \tag{94}$$

To solve this equation, one has to substitute for the concentration of the radicals on the right hand side. This may easily be done by assuming a steady state concentration of the caged radicals, $[R\cdot^{\alpha}]^{c}$ (equation 95), and for the "free" radicals, $[R\cdot^{\alpha}]$ (equation 96).

$$d[R\cdot^{\alpha}]^{c}/dt=0=k_1[RD][Br\cdot]-k^{D}_{-1}[R\cdot^{\alpha}]^{c}[DBr]^{c}-k_d[R\cdot^{\alpha}]^{c} \tag{95}$$

$$d[R\cdot^{\alpha}]/dt=0=$$
$$k_d[R\cdot^{\alpha}]^{c}-k_{-1}[R\cdot^{\alpha}][HBr]-k'_{-1}[R\cdot^{\alpha}][HBr_3]-k_2[R\cdot^{\alpha}][Br_2] \tag{96}$$

Solving for $[R\cdot^{\alpha}]^{c}$ from equation 95 (equation 97), (where

$[DBr]^c$ is the cage concentration of deuterium bromide), and substituting this value of $[R\cdot^{\alpha}]^c$ into equation 96 and solving for $[R\cdot^{\alpha}]$ gives equation 98. A similar

$$[R\cdot^{\alpha}]^c = k_1[RD][Br\cdot]/(k^D_{-1}[DBr]^c + k_d) \tag{97}$$

$$[R\cdot^{\alpha}] = k_d k_1[RD][Br\cdot]/ (k^D_{-1}[DBr]^c + k_d)(k_{-1}[HBr] + k'_{-1}[HBr_3] + k_2[Br_2]) \tag{98}$$

expression may be derived for $[R\cdot^{\gamma}]$. Substituting equation 98 and the corresponding expression for $[R\cdot^{\gamma}]$ into equation 94 gives expression 99, which assumes that the rate of diffusion of the isomeric radicals is the same. Under the conditions described above, this expression may be integrated (equation 100). The integration further assumes that the concentration of deuterium bromide in the solvent cage does not change during the reaction.

$$\frac{d[R^{\alpha}Br]/dt}{d[R^{\gamma}Br]/dt} = \frac{k_1k_2}{k_5k_6}\left(\frac{k^D_{-5}[DBr]^c + k_d}{k^D_{-1}[DBr]^c + k_d}\right)\left(\frac{k_{-5}[HBr] + k'_{-5}[HBr_3] + k_6[Br_2]}{k_{-1}[HBr] + k'_{-1}[HBr_3] + k_2[Br_2]}\right) \tag{99}$$

$$\frac{[R^{\alpha}Br]}{[R^{\gamma}Br]} = \frac{k_1k_2}{k_5k_6}\left(\frac{k^D_{-5}[DBr]^c + k_d}{k^D_{-1}[DBr]^c + k_d}\right)\left(\frac{k_{-5}[HBr] + k'_{-5}[HBr_3] + k_6[Br_2]}{k_{-1}[HBr] + k'_{-1}[HBr_3] + k_2[Br_2]}\right) \tag{100}$$

Combining equation 100 with equation 93 and a similar one for the γ-position simplifies equation 100 to expression 101.

$$C^{\alpha}_{\gamma} = \left(\frac{k^{D}_{-1}[DBr]^{c} + k_{d}}{k^{D}_{-5}[DBr]^{c} + k_{d}}\right) = \frac{k_1}{k_5}\left(\frac{[R^{\gamma}H]^{f} - [R^{\gamma}H]^{\circ} + [R^{\gamma}Br]}{[R^{\alpha}H]^{f} - [R^{\alpha}H]^{\circ} + [R^{\alpha}Br]}\right) \quad (101)$$

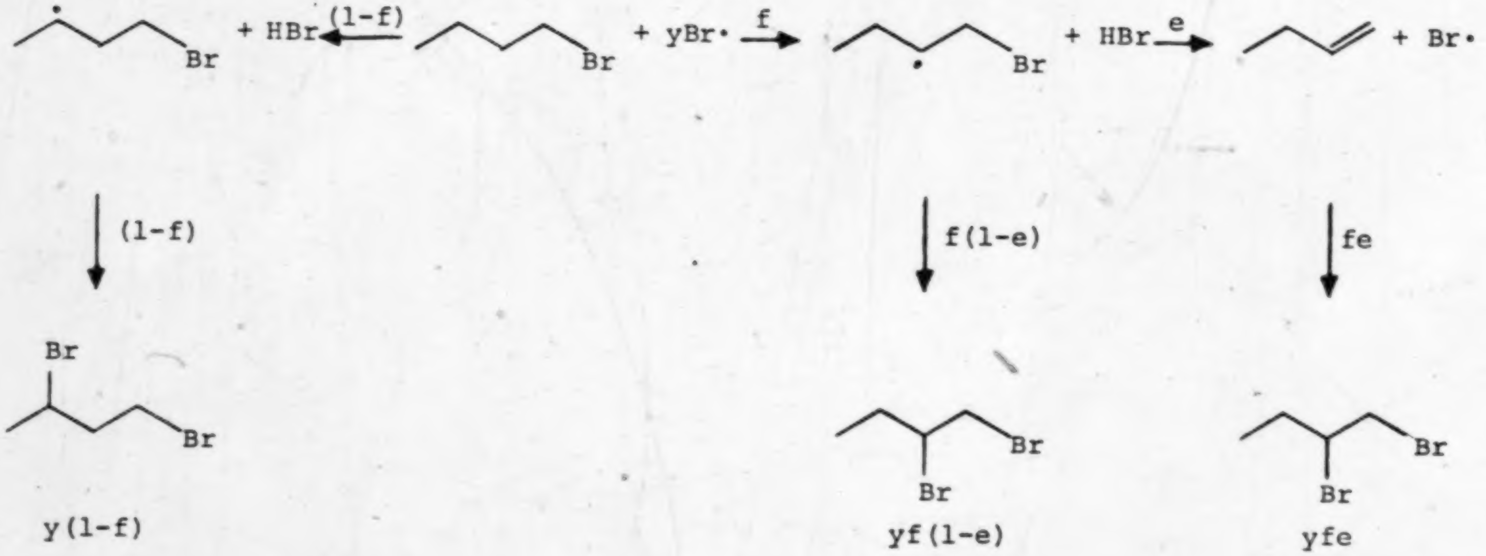
APPENDIX 2

Simulation of the Bromination of 1-Bromobutane-Br-82 with Molecular Bromine

The reaction of 1-bromobutane labelled with Br-82 with molecular bromine reported by Bruylant et al.[67] was simulated as shown in Scheme 7. Only the formation of three products was considered, 1,2-dibromobutane, 1,3-dibromobutane (representing all the non-vicinal dibromides) and hydrogen bromide. The reaction was simulated stepwise. In each step, y moles of Br· attack the molecule, and of these a fraction f abstracts the β-hydrogens. (Reversal with hydrogen bromide was assumed to have no effect on these figures, see below.) A fraction of the β-bromobutyl radicals, e, eliminates bromine atoms to give 1-butene, which then adds bromine to form 1,2-dibromobutane. The amount of each product formed is given in the scheme.

The program assumes that the values of f and e are constant with percentage reaction. The value for f was calculated as 0.8 from the data in the communication.[67] The value for e was varied from 0 to 1,

Scheme 7


Br
+ HBr
(1-f)
Br
+ yBr·
f
Br
+ HBr
e
+ Br·
(1-f)
f(1-e)
fe
Br
Br
y(1-f)
Br
Br
yf(1-e)
Br
Br
yfe

i.e. the amount of elimination from the β-bromobutyl radicals was changed from 0% to 100%. The reaction was simulated to 87% converson of the bromine; this figure was also determined from the published results. The reaction was simulated in 1000 steps, i.e. the value of y was set at 0.00087. Simulation using a larger number of steps, e.g. 10,000, was found to give the same results within the accuracy of the reported data.

In each step, the Br-82 that was eliminated was mixed with the bromine pool prior to any further reaction, and the ratio of radioactive to "dead" bromine in the pool determined. The radioactivity in each of the products formed in this step was then calculated and the results accumulated. The program is listed on the next page.

```
      IMPLICIT REAL*8 (A-H, O-Z)
      K=870
      E=0.0D0
      ALKYL=1.91D0
      WRITE(6,801)
  801 FORMAT('0CON.',6X,'ELIM',10X,'IN',
     X8X,'1,2-DI',7X,'OTHER',7X,'2-POS',6X,'1-POS')
      DO 2 I=1,101
      AMT=0.0D0
      ALK=ALKYL
      POOL=2.0D0
      Y=DFLOAT(K)/1000000.0D0
      RATIO=0.0D0
      ANON12=0.0D0
      DS12=0.0D0
      ELIM12=0.0D0
      POS2=0.0D0
      POS1=0.0D0
      F=0.80D0
      YFE=Y*F*E
      DO 1 J=1,1000
      RATIO=(YFE+AMT)/(POOL+YFE)
      ANON12=Y*(1.0D0-F)*(1.0D0+RATIO)+ANON12
      DS12=Y*F*(1.0D0-E)*(1.0D0+RATIO)+DS12
      ELIM12=2.0D0*YFE*RATIO+ELIM12
      POS2=Y*F*RATIO+POS2
      POS1=Y*F*(1.0D0+E*RATIO-E)+POS1
      ALK=ALK-Y
      POOL=POOL-Y
    1 AMT=RATIO*POOL
      KK=K/10
      TOTAL=ALKYL-ALK
      P12=100.0D0*(DS12+ELIM12)/TOTAL
      P13=100.0D0*ANON12/TOTAL
      PINORG=100.0D0*RATIO*POOL/TOTAL
      PER2=100.0D0*POS2/(POS1+POS2)
      PER1=100.0D0*POS1/(POS1+POS2)
      EE=100.0D0*E
      WRITE(6,910)KK,EE,PINORG,P12,P13,PER2,PER1
  910 FORMAT(' ',I3,F13.4,F11.1,5F12.1)
    2 E=E+0.01D0
      CONTINUE
      STOP
      END
```

APPENDIX 3

Mass Spectral Analysis of the Dibromides Formed in the Bromination with Bromine-81

A dibromide whose bromine atoms have isotopic ratios of bromine-79 : bromine-81 of a : b and a' : b' gives three peaks in the molecular ion region of the mass spectrum. The intensity of these molecular ions will be in the ratio aa' : (ab' + a'b) : bb'.[77] The Br-79 : Br-81 ratio for the molecule may be easily determined from the observed peak heights. Let the first peak height be p (≡ aa'), that of the second be q (≡ ab' + a'b) and that of the third be r (≡ bb'). The fraction of Br-79 in the two bromine atoms will be given by equation 102.

$$
\begin{aligned}
0.5\left(\frac{a}{a+b}+\frac{a'}{a'+b'}\right) &= \frac{0.5a(a'+b')+0.5a'(a+b)}{(a+b)(a'+b')} \\
&= \frac{0.5aa'+0.5ab'+0.5aa'+0.5a'b}{aa'+a'b+ab'+bb'} \\
&= \frac{aa'+0.5(ab'+a'b)}{aa'+(a'b+ab')+bb'} \\
&= \frac{p+0.5q}{p+q+r} \qquad (102)
\end{aligned}
$$

The isotopic ratio of each of the two bromine atoms may also be determined. The intensities of the second and third peaks relative to the first are given by equations 103 and 104 respectively. Multiplying

$$n = \frac{q}{p} = \frac{ab' + a'b}{aa'} = \frac{b'}{a'} + \frac{b}{a} \qquad (103)$$

$$m = \frac{r}{p} = \frac{bb'}{aa'} \qquad (104)$$

equation 103 by b/a and substituting for (bb'/aa') from equation 104 and rearranging gives the quadratic equation 105. Multiplying by b'/a' instead of by b/a

$$\left(\frac{b}{a}\right)^2 - n\frac{b}{a} + m = 0 \qquad (105)$$

gives the same expression as 105 with b'/a' instead of b/a. The Br-81/Br-79 ratio of the two bromine atoms is therefore given by the two roots of this quadratic equation.

Thus for the vapour phase photobromination of 1-bromobutane with bromine-81, 1,2-dibromobutane gave three peaks in the molecular ion region in the ratio 1 : 10 : 16 (m/e 214, 216, 218 respectively, see Table 21). The isotopic ratio of the two bromine atoms can therefore be calculated as in expression 106, and since

$$\frac{\text{Br-81}}{\text{Br-79}} = \frac{10 \pm \sqrt{10^2 - 4 \times 16}}{2} = 8,\ 2 \qquad (106)$$

$a + b = a' + b' = 1$ (by definition), $a = 0.33$, $b = 0.67$, $a' = 0.11$ and $b' = 0.89$.

To determine the amount of 1,2-dibromobutane that was formed by addition of bromine to 1-butene, it was assumed that the rate of formation of 1,2-dibromobutane was constant relative to that of 1,3-dibromobutane. Consequently, the 1,2-dibromobutane that was formed by direct substitution had the same Br-79/Br-81 ratio as 1,3-dibromobutane (viz 0.32:0.68, Table 21), while the 1,2-dibromobutane formed from the alkene had the same average isotopic ratio as the bromine in the 3-position of 1,3-dibromobutane (viz 0.15:0.85, Table 21). If the fraction of 1,2-dibromobutane formed from olefin was e, the final Br-79 content of this dibromide (0.22, Table 21) is given by equation 107, whence e = 0.59.

$$0.32(1 - e) + 0.15 = 0.22 \qquad (107)$$

APPENDIX 4

Photobromination of 1-Bromobutane in the Gas Phase

This reaction was studied by Dr. R. J. Arhart in these laboratories.

An aliquot (0.2 ml) of a 1.58 M bromine solution in 1-bromobutane was placed in a 5 l reaction bulb, which was then degassed and sealed. The reactants were allowed to vapourize in the absence of light and they were irradiated till all the bromine colour was discharged. The products were collected and analyzed by glpc (10 m x 5 mm and 6 m x 5 mm 10% DEGS on Diatoport S glass columns). Five products were detected. The first three were identified as 1,1-, 1,2- and 1,3-dibromobutane by comparison of their retention times with those of authentic materials. The last two products were collected by preparative glpc (2 m x 5 mm 10% DEGS on Diatoport S, glass column, 165°) and identified as 1,2,2- and 1,2,3-tribromobutane by comparison of their mass, ir and nmr spectra with those of the authentic materials. The product distribution that was obtained (1,1:1,2:1,3:1,2,2:1,2,3 = 0.14:2.36:1.00:0.21:3.43) was confirmed independently by this writer.

Preparation of 1,2,2-, 1,2,3- and 1,3,3-Tribromobutane

This work was carried out by Dr. R. J. Arhart in these laboratories.

1,2,3-Tribromobutane was prepared as described in section III.1, and it had the same spectral data as reported there.

1,2,2-Tribromobutane was collected by preparative glpc (2 m x 5 mm 10% DEGS on Diatoport S, 160°) from the products of the liquid phase photobromination of 1,2-dibromobutane. Its mass spectrum showed the parent peaks at m/e 292, 294, 296, 298 (ratio 1:3:3:1) and very intense P-Br peaks at m/e 213, 215, 217 (ratio 1:2:1). Its nmr spectrum (CCl_4, TMS external standard) showed three sets of absorption peaks, in accordance with its structure: τ 8.80 (t, J = 6.5 Hz, 3H), τ 7.51 (q, J = 7 Hz, 2H) and τ 5.75 (s, 3H).

1,3,3-Tribromobutane was presumed to be the major product from the vapour phase bromination of 1,3-dibromobutane. It was shown that this compound was not 1,2,2- or 1,2,3-tribromobutane by comparing its glpc retention time (2 m x 5 mm 10% DEGS) to that of these compounds. Its mass spectrum showed the parent peaks at m/e 292, 294, 296, 298 in a ratio of 1:3:3:1, as expected for a tribromide.

Photobromination of 1,2- and 1,3-Dibromobutanes

These reactions were studied by Dr. R. J. Arhart in these laboratories.

An aliquot sample (~ 0.05 ml) of a 0.8 M bromine solution in the dibromide was placed in a 5 l reaction bulb. After degassing, the substrates were allowed to vapourize and they were irradiated till all the bromine colour was destroyed. The products were collected and analyzed by glpc (2 m x 5 mm 10% DEGS on Diatoport S, 140°). 1,2-Dibromobutane gave two products, 1,2,2-tribromobutane (94%) and 1,2,3-tribromobutane (6%), while 1,3-dibromobutane gave three products in a ratio of 3.8:18.4:1.0 (in order of their elution times). The product with the highest retention time, that made up 4% of the three products, was 1,2,3-tribromobutane, identified by spiking with the authentic material.

Brominations with Bromine-81 in the Liquid Phase

These reactions (see Table 4) were run without any solvent, using 5:1 molar mixtures of substrate: bromine-81. The reactions were run in sealed, degassed Pyrex ampules, and were irradiated at 30° till all the bromine colour was discharged. After reaction, the products were collected by preparative glpc (dibromobutanes and *trans*-1,2-dibromocyclohexane on a 3 m x 5 mm 10% DEGS on Chromosorp W, metal column and *cis*-1-*trans*-2-dibromo-4-*tert*-butylcyclohexane on a 3 m x 5 mm 15% DIDP on Chromosorp W AW, glass column) and then submitted to mass spectral analysis to determine the ratio of the intensities of the parent peaks (see Table 4). In the bromination of *cis*-4-*tert*-butylbromocyclohexane, which was prepared as reported[44], with bromine-81, the hydrogen bromide that was formed was distilled by trap to trap distillation into a solution of cyclohexene in diethyl ether. The ether solution was shaken overnight at room temperature, and the bromocyclohexane formed was collected by preparative glpc (6 m x 5 mm 10% Carbowax on Chromosorp P AW, glass column) and analyzed by mass spectroscopy. The major product from this bromination reaction, *cis*-1-*trans*-2-dibromo-4-*tert*-butylcyclohexane, was identified by comparison of its spectral data with that of the authentic material prepared by the addition of bromine to 4-tert-butylcyclohexene (bp 78° (1.3 mm), n_D^{25} 1.5250; lit.[135] bp 68° (0.3 mm), n_D^{25} 1.5247). The nmr spectrum (CCl_4, TMS internal standard, Varian HA100) showed the characteristic equatorial hydrogens at τ 5.35 (base width 23 cps). Its ir spectrum agreed with that reported;[136] additional very small absorptions at 807 and 703 cm^{-1} indicated small amounts of the diequatorial isomer.

Reinvestigation of the Vapour Phase Photobromination of 1-Bromobutane

This work was carried out by Mr. T. C. S. Ruo in these laboratories since the completion of this thesis.

The bromination of 1-bromobutane (30.29×10^{-4} mol) with molecular bromine (61.00×10^{-5} mol) at ambient temperature was run in a 12 l reaction bulb. It was photolyzed until all the bromine colour was discharged and the products were collected in a liquid nitrogen trap. Eleven products were obtained: 1-bromo-2-butene (1.1%), 1,1-dibromobutane (1.8%), 1,2-dibromobutane (34.4%), 1,3-dibromobutane (13.0%), 1,2,2-tribromobutane (1.3%), 1,4-dibromo-2-butene (1.6%), 1,2,3-tribromobutane (27.4%), dl-1,2,3,4-tetrabromobutane (6.0%) and meso-

1,2,3,4-tetrabromobutane (11.2%). The compounds are listed in their order of elution from the glpc column used (6' x 1/4" 10% Carbowax 20 M TPA glass column). 1,2,3,4-Tetrabromobutane was obtained as a solid and quantitated by weighing the major portion of the solid and adding its weight to the small amount that was eluted from the glpc column. It was isolated and identified by comparison of its mass, nmr and ir spectra with those of the authentic material. Two other unidentified compounds were also detected; one was eluted from the glpc column after 1,2-dibromobutane (<0.9%) and the other one was eluted after 1,3-dibromobutane (<1.4%). The material balance based on bromine consumed was 100.1% when the two unidentified compounds (2.3%) were assumed to be unsaturated dibromides. This value agreed with the weight of the recovered material collected (98.4%).

APPENDIX 5

Determination of the Protium Content of Perdeuterio-1-chlorobutane by Mass Spectrometry

The mass spectrum of perdeuterio-1-chlorobutane shows a number of peaks in the parent peak region. The peak at m/e 101 (P_{101}) may be assigned to the following ions (equation 108). If A is the percentage of $C_4D_9Cl^{35}$

$$P_{101} = (C_4D_9Cl^{35})^+ +$$

$$(C_4D_8Cl^{37})^+ + (C_4C^{13}D_8HCl^{35})^+ + (C_4D_7H_2Cl^{35})^+ \qquad (108)$$

in the sample, B the percentage of $C_4D_8HCl^{35}$, C the percentage of $C_4D_7H_2Cl^{35}$, m the natural isotopic ratio of Cl^{37}/Cl^{35}, x the C^{13} contribution and y the fraction of species that lose a deuterium atom,* equation 108 may be rewritten as equation 109. A similar analysis of the

$$P_{101} = A + Amy + Bx + Cm = A(1 + my + \frac{B}{A}x + \frac{C}{A}m) \qquad (109)$$

peak at m/e 100 (P_{100}) gives equation 110.

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* Since y was small (0.148, determined from the mass spectrum of 1-chlorobutane under the same conditions), loss of a hydrogen atom instead of a deuterium atom was neglected.

$$P_{100} = B + Bmy + Cx = B(1 + my + \frac{C}{B}m) \tag{110}$$

The ratio of these two peaks will therefore be given by equation 111, which may be rearranged to give the ratio B/A (equation 112), the ratio of the

$$\frac{P_{101}}{P_{100}} = \frac{A}{B}\left(\frac{1 + my + \frac{B}{A}x + \frac{C}{A}m}{1 + my + \frac{C}{B}x}\right) \tag{111}$$

$$\frac{B}{A} = \frac{P_{100}}{P_{101}}\left(\frac{1 + my + \frac{B}{A}x + \frac{C}{A}m}{1 + my + \frac{C}{B}x}\right) \tag{112}$$

$C_4D_8HCl^{35}/C_4D_9Cl^{35}$ species. Equation 112 was solved for B/A in two ways.

In the first method, the values of m and x were obtained from the literature;[77] the value for y was determined from the mass spectrum of the natural protiated material run under the same conditions as perdeuterio-1-chlorobutane, assuming that there was no isotope effect on the loss of a hydrogen or a deuterium atom in the mass spectrometer. The ratio C/A was approximated by the ratio of the peaks at m/e 99 and 101 while C/B was approximated by the ratio of the peaks at m/e 99 and 100 in the spectrum of perdeuterio-1-chlorobutane. Equation 112 may then be rewritten as equation 113, which may be solved for the ratio B/A.

$$\frac{B}{A} = \frac{P_{100}}{P_{101}}\left(\frac{1 + my + \frac{B}{A}x + \frac{P_{99}}{P_{101}}m}{1 + my + \frac{P_{99}}{P_{100}}x}\right) \qquad (113)$$

In the second method, since x, y and c were small, the terms my, $\frac{C}{B}x$ and $\frac{C}{A}m$ would be even smaller, and hence may be neglected. Equation 112 then reduces to equation 114, which may be solved for B/A. The ratio

$$\frac{B}{A} \quad \frac{P_{100}}{P_{101}}\left(1 + \frac{B}{A}x\right) \qquad (114)$$

B/A calculated from equations 113 and 114 was the same within the limits of the accuracy of the mass spectral data.